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SECTION-A

PART II

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**Synthesis and characterization of transition metal complexes of isatin oxime**

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**Abstract**

The transition metal complexes of Co(II), Ni(II), Cu(II), Mn(II), Zn(II), Pb(II), Fe(II) and Fe(III) with isatin oxime (IHA) have been prepared in yields ranging from 60-70%. These complexes have been well characterised with the aid of elemental analyses, molar conductance, magnetic susceptibility, ESR, IR, Mass, FAB,  $^1\text{H}$  and  $^{13}\text{C}$  NMR studies.

(**Keywords** : transition metal complexes/magnetic & spectral studies/isatin oxime).

**Introduction**

Cyclic compounds like isatin, ninhydrin and their derivatives are known for their important biological activities<sup>1,2</sup>, applications in biochemical<sup>3</sup>, analytical<sup>4</sup>, industrial and various other fields<sup>5</sup>. Isatin oxime synthesised by condensation of isatin with hydroxyl amine was also found to have a number of applications and was found to undergo significant changes on complexation<sup>6-12</sup>. IHA complexes are selectively found to show considerable changes in biological activities on complexation<sup>13-18</sup> as compared to their pure ligand forms. In this paper we report the results of our investigations on the synthesis and structural behaviour of Co(II), Ni(II), Cu(II), Mn(II), Zn(II), Pb(II), Fe(II) and Fe(III) complexes of isatin oxime abbreviated as IHA (Fig. 1).



Fig. 1 – Structure of IHA, (I) keto form, (II) enol form.

### Materials and Method

All the solvents, the metal salts and the chemicals used were either of Analar grade or guaranteed reagents. Solvents such as methanol, ethanol, petroleum ether (40–60°C), chloroform, acetone, DMF, DMSO etc., were purified before use as per the reported procedures<sup>19</sup>. A 10% ethanolic ammonia solution was used for pH adjustment during the synthesis of metal chelates. IR spectrum of the ligand IHA was recorded in KBr phase on Perkin Elmer Model No. 435.

The metal contents of the complexes were analysed employing standard literature procedure<sup>20,21</sup>. Chloride was estimated by Volhard's method<sup>22</sup>.

The elements C, H and N in ligand and complexes have been analysed on a Perkin Elmer-240 C elemental analyser. IR spectra of complexes were recorded in KBr phase in the range of 4000–400  $\text{cm}^{-1}$  on Perkin Elmer Model No. 435.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of the ligands and Zn(II), Pb(II) and Hg(II) complexes in  $\text{CDCl}_3$  and  $\text{DMSO}-d_6$  using tetramethyl silane (TMS) as standard were recorded on Bruker WH 270 NMR spectrometer. ESR spectra of Cu(II) complexes were scanned on Jeol SE-3X (K band and Q band) instrument at room temperature. Magnetic susceptibilities of the metal complexes were measured at room temperature on a Faraday balance model 7550. Molar conductance was measured on a Digisun digital conductivity meter model D<sub>1</sub> 909 at room temperature with necessary calibration ( $1 \times 10^{-3}$  M solutions of IHA and complexes in DMSO). FAB spectrum of Cu(II) complex was recorded on VG Autospec-M mass spectrometer, using m-nitrobenzyl alcohol as the matrix in DMSO media.

*Preparation of ligand* : IHA was prepared by refluxing an ethanolic solution (50 ml) of isatin (8.5 g, 0.057 M) and hydroxylamine (4.0 g, 0.028 M) for ~45 min. The reaction mixture was cooled and left aside for 1 h. A yellow crystalline product was obtained. The product was filtered and recrystallised from ethanol. Yield 75%, m.p. 243°C (Found : C, 59.62; H, 3.72; N, 17.39  $\text{C}_8\text{N}_2\text{O}_2\text{H}_6$  Calcd. C, 59.25; H, 3.7; N, 17.28%). The ligand IHA



was characterised by Mass, IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. Molecular weight of the ligand from mass spectra was found to be 162.

*Preparation of the Complexes* : M(II)-IHA complexes [M(II) = Co(II), Ni(II), Cu(II), Mn(II), Zn(II), Pb(II), Fe(II) and Fe(III)] were prepared by mixing together the ethanolic solution (20 ml) of IHA (0.5 g, 0.01 M) and the appropriate metal salt solution (0.25 g, 0.005 M). The complexes which were precipitated by refluxing the reaction mixture for 13-15 h and raising pH of the solution to  $\sim 7$ , were filtered, washed with methanol, ethanol and double distilled water followed by petroleum ether (40–60°C) and finally dried over fused calcium chloride in a vacuum desiccator at room temperature.

### Results and Discussion

In IR spectrum of IHA the peaks appeared at 3180, 3050, 2896 and 1713  $\text{cm}^{-1}$  correspond to  $\nu\text{N-OH}$ ,  $\nu\text{N-H}$ ,  $\nu\text{C-H}$  and  $\nu\text{C=O}$  respectively.  $^1\text{H}$  NMR spectrum of the oxime at 24°C in  $\text{CDCl}_3$  + 3 drops of  $\text{DMSO-d}_6$  shows peaks at  $\delta$  13.2 ppm (1H, enolic -OH),  $\delta$  10.59 ppm (1H, =N-OH) and  $\delta$  7.30–8.47 ppm (4H, Ar-H). The  $^{13}\text{C}$  NMR spectrum of IHA showed 8 signals indicating the presence of 8 carbons. It showed peaks at  $\delta$  164 ppm (-CO-), two peaks at  $\delta$  142, 144 ppm (-C=N-OH, -N=C-OH) and five peaks at  $\delta$  110, 116, 123, 127 and 133 ppm (aromatic carbons).

It is evident from  $^1\text{H}$  NMR that IHA exists in both keto and enol forms<sup>23</sup> (Fig. 1). The integration of  $^1\text{H}$  NMR peaks reveals that enol form (II) exists in higher percentage than keto form (I, Table 1). The metal complexes of IHA are insoluble in organic solvents but slightly or fairly soluble in DMF and DMSO.

The values of molar conductance of the complexes in DMF at 0.001 M concentration lie in the range of 4-13  $\text{Mho cm}^2 \text{mol}^{-1}$  suggesting that they are nonionic in nature<sup>24</sup>.

*Magnetic moments* : The observed magnetic moments for Cu(II)-IHA complex is 1.20 BM indicating either distorted octahedral or square planar geometry<sup>25-27</sup>. The observed value of 3.48 BM in Ni(II)-IHA complex is greater than spin value. This is because of larger orbital splitting of the  $^3\text{T}_1$  term of tetrahedral bivalent nickel complex resulting in a low symmetry ligand field component. The observed magnetic moment value of Co(II) complexes in general lies in the range of 3.87–4.48 BM for tetrahedral geometry. In Co(II)-IHA complex this value is 2.56 BM which is lower than expected range. This may be due to extensive spin orbit coupling. Magnetic moment values of Mn(II)-IHA and Fe(III)-IHA complexes are 4.84 BM and 4.78 BM, respectively, which are lower than the expected range.

**ESR spectra :** The  $g$  factor in general is anisotropic in Cu(II) complexes because of tetragonal distortion. In such complexes,  $g$  factor is given by equations  $g_{\parallel} = 2.0023 - 8\lambda/E_0 - E_2$  and  $g_{\perp} = 2.0023 - 2\lambda/E_0 - E_3$ . The values of  $(E_0 - E_2)$  and  $(E_0 - E_3)$  can be obtained from absorption spectrum. The ESR spectrum of Cu(II)-IHA complex showed three  $g$  values indicating anisotropy. The  $g_x$ ,  $g_y$  and  $g_z$  values at 2.2636, 2.0813, 2.0211, respectively, indicate lower symmetry at the metal ion<sup>28-30</sup>.

**<sup>1</sup>H NMR spectra :** The presence of signal at  $\delta$  13.2 ppm in the NMR spectrum<sup>31</sup> of IHA indicates the existence of keto enol tautomerism. The peaks corresponding to enol

form  $\begin{pmatrix} \text{OH} \\ | \\ -\text{C}=\text{N} \end{pmatrix}$  and amide ( $-\text{NH}$ ) protons are not observed in <sup>1</sup>H NMR spectra<sup>31</sup> of Zn(II) and Pb(II)-IHA complexes indicating deprotonation *via* enolisation upon complexation. The signals of aromatic protons of the ligands are also shifted from the range of  $\delta$  7.30–8.47 to  $\delta$  6.30–8.00 in the complexes due to increased shielding effect because of transfer of electrons from donor sites of the ligand to empty metal orbitals. The signal for oxime proton observed at  $\delta$  10.59 ppm in the ligand is shifted to  $\delta$  10.40 ppm in the complexes. This clearly indicates the participation of nitrogen of oxime and oxygen of  $-\text{OH}$  through deprotonation *via* enol form in bond formation resulting in a stable five membered ring structure.

**IR spectra :** It is evident from IR spectra<sup>32,33</sup> of all the complexes (Table 1) that the enolic proton is lost on complexation and the  $\nu$ -NH stretching frequency observed at 3050  $\text{cm}^{-1}$  in the ligand, is missing in all the complexes except in Cu(II)-IHA complex. Further as a result of complexation an extra peak in the region of 1139–1196  $\text{cm}^{-1}$  appears which corresponds to C-O stretching frequency<sup>32</sup>. This clearly indicates the deprotonation of proton from oxygen of  $-\text{OH}$  group *via* enol form of the ligand. Due to this, the absorption peak of  $\nu\text{C}=\text{O}$  at 1713  $\text{cm}^{-1}$  of the ligand is missing in all the complexes except Cu(II) complex. This also indicates that the enol form of ligand takes part in complexation. From the equilibrium studies it is revealed that there is clear evidence of deprotonation upon complexation and the presence of one dissociable proton.

In Cu(II)-IHA complex, it is observed that the ligand takes part in complexation in its keto form only, which is due to complexation at low pH. This is also confirmed from its IR spectrum by the presence of  $\nu$  - NH (3050  $\text{cm}^{-1}$ ) and  $\nu$  C=O (1695  $\text{cm}^{-1}$ ) peaks.

Apart from this, the IR spectra of all the complexes show a considerable shift in the stretching frequency of oxime  $\nu\text{C}=\text{N}$  (Table 1), which indicates that the nitrogen of oxime group participates in coordination. Based on this we confirm that oxygen of enolic form

Table 1 – IR data and  $^1\text{H}$  NMR data of IHA and its metal complexes.

Ligand/ Complex	IR (KBr) cm <sup>-1</sup>								$\delta$ HOH/OH
	Oxime $\nu_{\text{N-OH}}$	amide $\nu_{\text{NH}}$	Carbonyl $\nu_{\text{C=O}}$	aromatic $\nu_{\text{C-H}}$	oxime $\nu_{\text{C=N}}$	Complex $\nu_{\text{C=N}}$	$\nu_{\text{HOH}}$		
IHA	3180	3050	1713	2896	1661	--	--	--	
Co(II)	3160	--	--	2890	1664	1616	3212	1600 1286	
Ni(II)	3165	--	--	2890	1668	1616	3379	1600 1231	
Cu(II)	3165	3050	1695	2890	1667	--	3300	1602 1223	
Mn(II)	3160	--	--	2896	1679	1612	3200	1605 1201	
Zn(II)	3160	--	--	2919	1646	1598	3334	1602 1225	
Pb(II)	3164	--	--	2830	1690	1617	3215	1605 1213	
Fe(II)	3150	--	--	2860	1665	1618	3409	1600 1213	
Fe(III)	3160	--	--	2919	1666	1616	--	--	

 $^1\text{H}$  NMR of IHA:  $\delta$  13.2 (1H, enolic -OH),  $\delta$  10.59 (1H, =N-OH),  $\delta$  7.30-8.47 (4H, Ar-H),  $\delta$  2.60 (1H, -NH).Zn(II)-IHA :  $\delta$  6.30-8.00 (4H, Ar-H),  $\delta$  10.40 (1H, =N-OH).Pb(II)-IHA :  $\delta$  6.80-7.97 (4H, Ar-H),  $\delta$  10.40 (1H, =N-OH).

Table 2 – Physical and analytical data of IHA and its complexes.

Sl. No.	Ligand / Complex	Empirical Formula (Formula Wt.)	Colour	M.P. (°C)	$\mu_{\text{eff}}$ (BM)	Analysis Found (Calcd.) %				Molar conductivity (Mho.cm <sup>2</sup> .mol <sup>-1</sup> )
						C	H	N	M	
1.	IHA	C <sub>8</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub> (162)	Dark yellow	243	--	59.62 (59.25)	3.72 (3.70)	17.39 (17.28)	--	--
2.	[Co(IHA) <sub>2</sub> ].H <sub>2</sub> O	[Co(C <sub>8</sub> H <sub>5</sub> N <sub>2</sub> O <sub>2</sub> ) <sub>2</sub> ].H <sub>2</sub> O (398.91)	Brown	Dp	2.56	47.32 (48.13)	2.59 (2.50)	14.48 (14.03)	11.08 (11.77)	10
3.	[Ni(IHA).Cl].4H <sub>2</sub> O	[Ni(C <sub>8</sub> H <sub>5</sub> N <sub>2</sub> O <sub>2</sub> ).Cl].4H <sub>2</sub> O (582.4)	Light green	Dp	3.48	33.93 (32.96)	3.57 (3.09)	9.97 (9.61)	17.81 (19.16)	13
4.	[Cu(IHA) <sub>2</sub> .Cl <sub>2</sub> ].H <sub>2</sub> O	[Cu(C <sub>8</sub> H <sub>5</sub> N <sub>2</sub> O <sub>2</sub> ) <sub>2</sub> .Cl <sub>2</sub> ].H <sub>2</sub> O (476.5)	Dark green	Dp	1.57	39.59 (40.29)	2.92 (2.93)	11.10 (11.75)	12.22 (13.32)	7
5.	[Mn(IHA) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].2H <sub>2</sub> O	[Mn(C <sub>8</sub> H <sub>5</sub> N <sub>2</sub> O <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ].2H <sub>2</sub> O (448.9)	Black	Dp	4.84	43.28 (42.77)	2.97 (3.11)	12.72 (12.47)	11.72 (12.23)	4
6.	[Zn(IHA).Cl].2H <sub>2</sub> O	[Zn(C <sub>8</sub> H <sub>5</sub> N <sub>2</sub> O <sub>2</sub> ).Cl].2H <sub>2</sub> O (55.9.76)	Yellow	Dp	Dia	35.95 (34.30)	2.47 (2.50)	10.38 (10.00)	22.54 (23.36)	10
7.	[Pb(IHA) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	[Pb(C <sub>8</sub> H <sub>5</sub> N <sub>2</sub> O <sub>2</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]	lemon yellow	Dp	Dia	35.35 (34.01)	2.10 (2.47)	10.52 (9.90)	38.05 (36.65)	9
8.	[Fe(II)IHA .Cl].2H <sub>2</sub> O	[Fe(II)(C <sub>8</sub> H <sub>5</sub> N <sub>2</sub> O <sub>2</sub> ).Cl].2H <sub>2</sub> O (540.69)	Orange	Dp	--	35.35 (35.51)	2.62 (2.59)	10.38 (10.35)	20.41 (20.65)	11
9.	[Fe(III)(IHA) <sub>2</sub> .Cl]	[Fe(III)(C <sub>8</sub> H <sub>5</sub> N <sub>2</sub> O <sub>2</sub> ) <sub>2</sub> .Cl] (413.3)	Orangish brown	Dp	4.78	44.59 (46.45)	2.86 (2.42)	12.65 (13.55)	14.26 (13.51)	7

Dp : Decomposes; Dia : Diamagnetic

of the ligand and nitrogen of oxime takes part in bond formation forming a stable five membered chelate ring.

**Elemental analysis :** Elemental analysis and metal ion analysis show the metal to ligand ratio in all the complexes IHA with Ni(II), Zn(II) and Fe(II) as 1:1, while in complexes of Co(II), Mn(II), Cu(II), Pb(II) and Fe(III) as 1:2. In all complexes except in Co(II), Mn(II) and Pb(II) the presence of chloride is indicated by Volhards test. Physical, analytical, magnetic and spectral data of complexes are compiled in Tables (1 & 2).

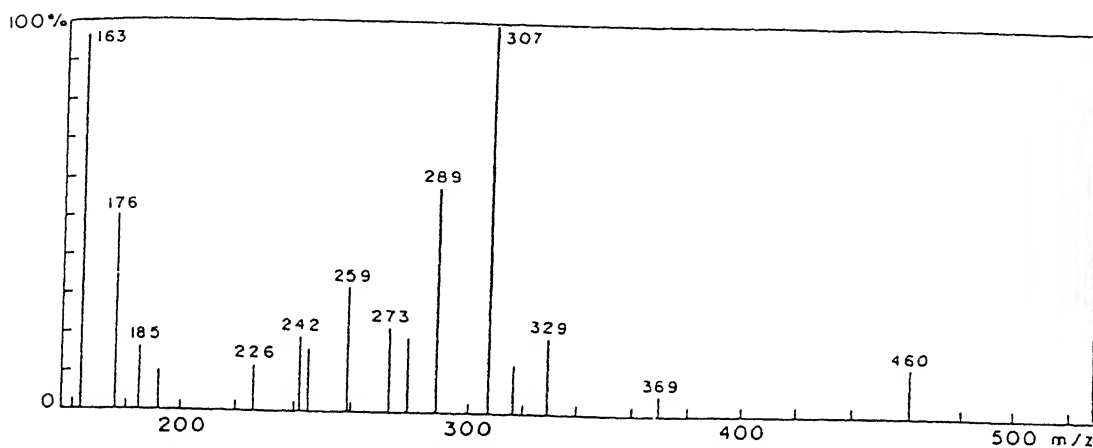
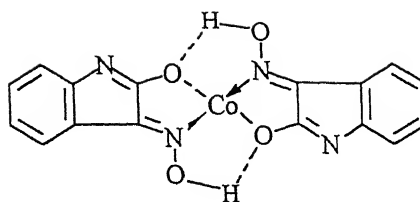
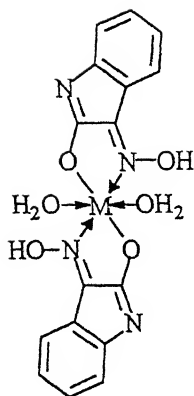
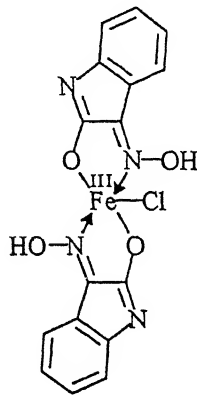
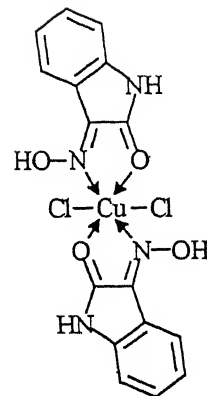
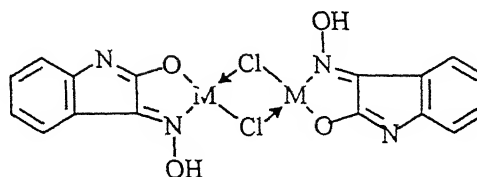


Fig. 2 - FAB spectrum of Cu(II)-IHA complex.

**Fast atom bombardment studies :** FAB studies<sup>34-37</sup> (Fig. 2) on Cu(II)-IHA complex further confirmed the composition of complex as 1:2 ( $m/z$  460). The composition of the complex is in agreement with elemental analysis and thermal analysis data.

**Thermogravimetric analysis :** Co(II), Ni(II), Cu(II) and Mn(II)-IHA complexes were studied by recording thermogravimetric curves, rate conversion curves and SDTA-curves<sup>38</sup>. It is observed from this data that in Co(II) and Cu(II)-IHA complexes there is one lattice water molecule (weight loss at 98° and 158°C respectively) with 1:2 metal to ligand composition. In Ni(II)-IHA complex these results reveal the metal to ligand composition of 1:1 with binuclear composition and four lattice water molecules (weight loss at 160°C). In Mn(II)-IHA complex the result indicates, the presence of two coordinated water molecules (weight loss in temperature range of 190–223°C) and two lattice water molecules (weight loss in temperature range of 50–159°C) with 1:2 metal to ligand composition. All these results are in agreement with the data obtained from elemental analyses and IR data. A broad peak in the range of 3200–3600  $\text{cm}^{-1}$  in IR spectra of complexes indicate the presence of water molecules substantiate the TGA findings. In addition to this, the presence of lattice

**Fig.3 : Co(II)-IHA complex** $M(II) = Mn(II), Pb(II)$ **Fig.4: Mn(II), Pb(II)-IHA complexes****Fig.5: Fe(III)-IHA complex****Fig.6: Cu(II)-IHA complex** $M(II) = Ni(II), Zn(II), Fe(II)$ **Fig.7: Ni(II), Zn(II), Fe(II)-IHA complexes**

- Fig. 3 – Proposed structure of Co(II)-IHA complex.  
 Fig. 4 – Proposed structures of Mn(II), Pb(II)-IHA complexes.  
 Fig. 5 – Proposed structure of Fe(III)-IHA complex.  
 Fig. 6 – Proposed structure of Cu(II)-IHA complex.  
 Fig. 7 – Proposed structures of Ni(II), Zn(II), Fe(II)-IHA complexes.

as well as coordinated water molecules in complexes is supported by peaks in the range of  $600\text{--}400\text{ cm}^{-1}$  and  $650\text{--}880\text{ cm}^{-1}$ , respectively.

Based on all these results from FAB, TGA, elemental analysis and spectral data, structures (Fig. 3-7) have been tentatively assigned for M(II)-IHA complexes. In Cu(II) complex of IHA (Fig. 6) since the complex formation takes place at very low pH, immediately on adding metal ion solution to the ligand solution, it is assumed that ligand takes part in complex formation in keto form without deprotonation which is further confirmed also from IR data and elemental analyses.

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## Synergic extraction and trace determination of vanadium(V) as ternary chelate with cinnamohydroxamic acid and thiocyanate in mibk and its application

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### Abstract

A highly sensitive, selective and rapid solvent extraction procedure for spectrophotometric method of determination of subtrace amount of vanadium(V) in methyl isobutylketone has been reported in this paper. Vanadium (V) is extracted with N- cinnamohydroxamic acid (N-CHA) and a mixed ligand thiocyanate (SCN) as a violet coloured complex in solvent phase at 1.8 M HCl. The ternary complex absorbs maximum at 555 nm. The system obeyed Beer's law from 0.4 to 12 ppm with optimum range of determination 1-9 ppm of V(V). The molar absorptivity and Sandell's sensitivity are  $0.745 \times 10^4 \text{ l.mole}^{-1} \text{ cm}^{-1}$  and  $6.8 \text{ ng cm}^{-2}$  of V(V) at 555 nm. A large number of cations and anions do not interfere. The method shows high selectivity with thiouriede as masking agent and it is simple, rapid, reproducible and reports high precision. The R.S.D. value is  $\pm 0.0012$  for average of seven determinations. The photometric determinations are also reported in detail and the standard deviations are minimal. The R.S.D. values are different for the steel (0.08%), rock (2-3%) and ore (2%) samples.

(**Keywords** : synergic extraction/ternary chelate/vanadium/N- CHA/SCN).

### Introduction

Extensive and all major efforts have been made to substitute either way of increasing the potential complexing power of hydroxamic acid group for trace determination of vanadium metal precisely, accurately and with equal fold of simplicity and rapidity. A secondary reagent has also been used to enhance the absorptivity. Thiocyanate claimed to be the effective ternary complex former group with donor nitrogen. All these observations are based on the question of selectivity of the methods largely developed by solvent extraction technique. Hydroxamic acids produced largely intense color, sharp maxima, sensitivity, high selectivity than its hydroxylamine counter groups with the metal. Moreover, the complexes have higher stability constants as compared to the hydroxylamine because of its higher metal : reagent ratios (1:3 and 1:4) previously cited for some complexes. Even

with 1:2 compositions the stability constant values for hydroxamic acids are greater than the hydroxylamines. It has been further observed that the  $k_2$  is greater than  $k_1$  with hydroxamic acid complexes whereas  $k_1$  is greater than  $k_2$  with hydroxylamines even in synergic extraction. The substitution by unsaturation linked directly hydroxamate group produced improved sensitivity and selectivity for extraction of V(V) in mibk. Synergic extraction<sup>1-3</sup> and ternary complexation<sup>4-6</sup> in photometry have been reported in literature. Synergic extraction with thiocyanate has also been described.

This paper reports the use of thiocyanate in synergic extraction of V(V) with cinnamohydroxamic acid at 1.8 M HCl. Environmental and real samples e.g. steel and rock have been analyzed for trace vanadium with high precision with minimal standard deviations.

## Materials and Method

### Reagents

*CHA solutions (0.031 M)* : The reagent was prepared in the usual way as reported earlier. 5 ml of 0.5% reagent solutions in methyl isobutyl ketone were used for the extraction.

*Ammonium vanadate solution* : Prepared by dissolving ammonium metavanadate in doubly distilled water containing a little ammonia and standardized by complexometric titration and photometrically with N-benzoylphenyl-hydroxamic acid. The solution was diluted to 100 µg/ml.

*Ammonium thiocyanate solution (0.26M)* : Prepared in doubly distilled water and standardized by Volhard's method. A 2% solution was used and diluted as necessary.

Exactly 0.1M hydrochloric acid was obtained by diluting stock standard 6M acid. A standard buffer of pH 4.0 was prepared from 0.2M acetic acid and 0.2M sodium acetate. All other chemicals used were general or analytical reagent grade and the solvents were purified.

*Procedure* : Take an aliquot of the vanadium(V) solution 0- 100 µg/ml ( $\sim 10^{-3}$ M) into a 50-ml separatory funnel and add 5ml of 0.5% N-CHA-reagent solution and 3 ml of 6M hydrochloric acid and dilute to give 10ml of the aqueous phase. Extract the wine red chelate formed at 1.8M HCl for 5 min with 10ml of methylisobutyl ketone as organic phase. Now add to the mixture 5ml of 2% ammonium thiocyanate and maintain the acidity of the medium. Maintain the volume of the aqueous phase at 15ml. Extract the violet coloured complex after shaking the mixture for 5 min with mibk. Dry the combined extract over

anhydrous sodium sulphate in a 50-ml beaker and combine the extracts and transfer them to a 25ml flask. Make up to 25ml with the pure solvent mibk. Prepare a reagent blank similarly. Measure the absorbance at 555 nm against solvent blank. Construct a calibration curve and run the unknown solution.

#### *Procedure for rock (mineral) analysis*

*Analysis of Ilmenite* : 0.5g of finely powdered sample (200-mesh) with 9g of potassium bisulphate and a few drops of sulphuric acid in silica crucible to a clear melt. Cool the mass and leach it with sulphuric acid (1+9). Boil and oxidize the solution with a few drops of nitric acid and then precipitate iron and titanium as hydroxides with an excess of 15% sodium hydroxide solution. Free any adsorbed vanadium from the hydroxide precipitate by double precipitation. Combine the filtrates and evaporate to about 50 ml. Transfer the solution to 10 ml standard flask and make up to volume with water.

Take appropriate aliquots of the solution and determine the vanadium content by the procedure using 15 mg of fluoride masking agent for any traces of iron and titanium in the solution.

*Procedure for steel analysis (BAS, 64b)* : Dissolve 0.5 gm of steel sample in 20 ml of dilute sulphuric acid (1:4) and digest it on a hot plate to a syrupy solution repeating the addition of acid. Treat it with 5 ml of conc. nitric acid for complete digestion. Evaporate it on a hot plate until medium strong fumes of sulphur trioxide are evolved. Dilute the solution with 50 ml water, boil and filter through Whatman no. 42 and wash the residue several times with hot acidulated ( $\text{H}_2\text{SO}_4$ ) water and finally with hot water. Collect the filtrate and washings in a 250 ml volumetric flask and make up to the mark. Transfer an aliquot of steel solution (5 ml) and oxidise it at room temperature with 0.1%  $\text{KMnO}_4$  solution till the pink colour persists. Add the solution to a hot 15 per cent sodium hydroxide solution and then boil the mixture. Filter off the precipitate and redissolve it in dilute hydrochloric acid. Reprecipitate the metal hydroxide again and filter. Combine the filtrates obtained by double precipitation technique and boil down to a low volume. Cool the solution and determine the vanadium content following the recommended procedures. Measure the absorbances of the extract solutions of 505 and 555 nm for the respective complexes and determine the metal content separately.

#### *Procedure for ore analysis*

*Analysis of Bauxite* : Fuse 0.5 g of the sample for 2h with sodium carbonate (3g) and sodium hydroxide (1g) in a nickel crucible. Cool the melt, leach with hot water and keep overnight. The aqueous extract contains vanadium and other insoluble materials along with iron and titanium. Filter the solution through Whatman No. 42, transfer into a 100-ml

olumetric flask and make up the volume with distilled water. Take an appropriate amount of the solution and determine the vanadium content by the above procedure.

### Results and Discussion

**Absorbance Spectra :** The absorbances of the mixed-ligand complex V(V)-CHA-SCN with 4 ppm of the metal in ternary extract were measured from 400 nm to 700 nm of spectral range. The complex absorbs maximum at 555 nm against solvent blank. The binary complex has been initially extracted at 1.8 M HCl without adding thiocyanate. Otherwise, the peak height is decreased and time of extraction needed is much higher. It is then further equilibrated in presence of added 0.26 M ammonium thiocyanate solution. Both the position and peak height have been changed and a bathochromic shift in  $\lambda_{\text{max}}$  by 30 nm have indicated mixed-ligand complex formation reaction. But the complex formation and absorption peak depend much on the concentration of thiocyanate ion and mode of addition of two reagents.

**Effect of acidity, reagent and thiocyanate :** The organic extract showed constant maximum absorbance in the optimum range of 0.5-2.5M HCl. Hence, all the extractions have been carried out at a fixed 1.8 M HCl medium. The mode of addition of the reagents, thiocyanate and acid has been found independent of the acidity maintained for extractions. The binary vanadium(V)-N-CHA complex has been initially extracted at this acidity and then ternary extraction was performed in presence of thiocyanate ion. It has been found that 2 ml of 0.5% (w/v) reagent solution was sufficient to produce the maximum colour intensity. The optimum concentration range needed for complete extraction was found to lie within 2 ml and 10 ml of 0.5% reagent solution. 5 ml of 0.5% CHA reagent was always added. The optimum range of concentration has been found to lie within 1 ml of 2% of  $\text{NH}_4\text{SCN}$  solution. 5.0 ml of 2.0% thiocyanate solution was always added in this ternary extraction method.

**Period of extraction and stability :** The % extraction was maximum with a water : MIBK ratio of 10:10 (v/v). The time for complete extraction of the violet vanadium species was found 5-6 min. The ternary complex was found stable for 24 h at room temperature.

**Beer's law, optimum range, absorptivity and sensibility :** The complex followed Beer's law over the concentration range 0-12 ppm of V(V). The Ringbom's plot for the ternary system have shown the optimum concentration range of determination to be 1 to 9 ppm of the metal. The percent (%) relative photometric error per 1% absolute photometric error was obtained from Ayre's plot to be 2.71. The molar absorptivity according to IUPAC nomenclature and the Sandell's sensitivity are  $7.45 \times 10^3 \text{ l.mole}^{-1} \cdot \text{cm}^{-1}$  and  $0.0068 \mu\text{g cm}^{-2}$  ( $6.8 \text{ ng cm}^{-2}$ ) of V(V).

Table 1 – Effect of diverse ions and the tolerance limit on the determination of 4 ppm vanadium (V) in mibk in presence of interfering ions.

Ions	Tolerance limit	Ions	Tolerance limit
		Fe (III)	N.I. <sup>a</sup>
EDTA	120	Cr (III)	160
Acetate	1000	Re (IV)	20*
Tartrate	1000	Al (III)	320
Citrate	1000	Zr (IV)	60*
Oxalate	140	Nb (V)	20*
Phosphate	300		
Fluoride	1500	Ta (V)	40*
Nitrate	3000	Ti (IV)	60*
Sulphate	3000	Th (IV)	320
Zn (II)	400	Mo (VI)	60*
Pb (II)	400	W (VI)	20
Ca (II)	400	U (VI)	160
Co (II)	320	Pd (II)	120
Ni (II)	320		

\* Fluoride masking

a No. Interference – Int. removed by double precipitation as hydroxides and subsequent fluoride masking.

The standard deviation (S.D.) and the relative standard deviation (R.S.D.) is found to be  $\pm 0.0063$  and  $\pm 0.0012$ , respectively based on the average of seven measurements and determinations (The maximum value of absorbance with 4 ppm of vanadium (V) is 0.585). 0.1 ppm (100 ppb) can be easily measured with the spectrometer. The R.S.D. values for spectrometric analysis are given in the Table 3.

The limit of detection is calculated by Youden's method. Here, the reagent absorbance is almost nil and measured absorbance is reported against solvent blank. Thus, the  $L_x$  value is given by the relation  $L_x = \bar{X} \pm 36 = 0.02 \text{ ppm} = 20 \text{ ppb}$  and the limit of determination has been calculated to be  $L_D = \bar{X} \pm 106 = 0.06 \text{ ppm} = 60 \text{ ppb}$ . The correlation co-efficient and co-efficient of variation (C.V.) are .9943, .9604, .9165, .9408 and 1.08 for all four samples, respectively. The corresponding  $t$ -values are 81.6, 11.9, 5.25, 7.7, 38.06 respectively.

Table 2 – Comparison of the present method with other methods.

Sl. No.	Aqueous condition	Solvent	Sandell's sensitivity $\mu\text{g cm}^{-2}/$ Molar absor- ptivity, $l.$ $\text{mole}^{-1} \cdot \text{cm}^{-1}$	Interfering metal ions
1.	$\text{V}^{\text{V}}$ , acidic medium, ben- zohydroxamic acid	1-Hexanol 450	0.012, $4.24 \times 10^3$	$\text{Fe}^{\text{III}}, \text{Bi}^{\text{III}}$ $\text{Al}^{\text{III}}, \text{Sn}^{\text{II}}$ $\text{Ti}^{\text{IV}}, \text{Zr}^{\text{IV}}, \text{W}^{\text{IV}}$
2.	$\text{V}^{\text{V}}$ , 0.7 M HCl, sodium sulphite	Isobutyl methyl ketone 430	0.0088, $5.73 \times 10^3$ 0.003	$\text{Zr}^{\text{IV}}, \text{Al}^{\text{II}}, \text{Fe}^{\text{III,II}}$
3.	$\text{V}^{\text{V}}$ , $\text{HClO}_4$ , persulphate acetone, ammonium acetate, pH 3-3.5, 1-(2- pyridylazo)-2-naphthol (PAN), waiting time 5 min.	Chloroform 615	$1.69 \times 10^4$	$\text{Cu}^{\text{II}}, \text{Fe}^{\text{II}}, \text{Ni}^{\text{II}}$ $\text{Cr}^{\text{VI}}, \text{Co}^{\text{II}}$ $\text{Bi}^{\text{III}}, \text{U}^{\text{VI}}$
4.	Present method $\text{V}^{\text{V}}$ , N-CHA, SCN	MIBK	0.0068 $7.45 \times 10^3$	N. Int.
5.	$\text{V}^{\text{V}}$ , pH 3.5-4.5 hydrazone compounds	–	0.0033 $1.54 \times 10^4$	$\text{Fe}^{\text{II, III}}$ $\text{Co}^{\text{II}}, \text{Pd}^{\text{II}}$
6.	$\text{V}^{\text{V}}$ , pH 3.5–4.5	0.2% oxine chloroform 550	0.016 $3.18 \times 10^3$	$\text{Mo}^{\text{VI}}, \text{U}^{\text{VI}}, \text{W}^{\text{VI}}$ $\text{Ti}^{\text{IV}}, \text{Bi}^{\text{III}}, \text{Cu}^{\text{II}}$ $\text{Fe}^{\text{III}}$
7.	$\text{V}^{\text{V}}$ , pH 1.9-2.8, 0.1% Benzoylphenylhydroxy- lamine	1-Hexanol, 450 Chloroform 415	0.012 $4.24 \times 10^3$	$\text{Fe}^{\text{III}}, \text{Bi}^{\text{III}}$ $\text{Sb}^{\text{III}}, \text{Al}^{\text{III}}$ $\text{Sn}^{\text{II}}, \text{Ti}^{\text{IV}}, \text{Zr}^{\text{IV}}$ $\text{Mo}^{\text{VI}}, \text{W}^{\text{VI}}, \text{Fe}^{\text{II}}$

Table 3 – Spectrometric determination of trace vanadium in steel, minerals and ores by ternary extraction in chloroform with cinnamohydroxamic acid and thiocyanate as synergic reagents and statistical analysis. Analysis of Environmental and real samples (Steel and rock ores)

Sample	Vanadium in sample (%)		Error (%)	Standard deviation and % RSD; <i>t</i> -value and correlation, co-efficient, <i>r</i>
	Found	Certified		
BAS Steel 64b	1.973	1.99	0.0175	± 0.0015
	1.925			± 0.08
	1.960			81.6, 0.9998
Ilmenite I	0.083	0.10	0.0167	± 0.0025
Hornbendite Rock	0.085			± 3
	0.081			11.9, 0.9604
Ilmenite II	0.140	0.15	0.0085	± 0.0030
	0.141			± 2
	0.143			5.25, 0.9165
Bauxite (Ore)	0.221	0.2	0.032	± 0.0050
	0.224			± 2
	0.220			7.7, 0.9408

Except Seel, *t*-value = 38.04 as *r* = 0.9871 in regression analysis.

#### Detection Limit

System	Corr. co-efficient	Students <i>t</i> value	Average (blank $\bar{x}$ )	Standard deviation blank $S_b$	Detection Limit PPb or $\mu\text{g/L}$		
					S	Youden	IUPAC
V(V)-N-	0.491	1.26	0.004	0.0052	6.9	20	7
CHA-SCN							

Detection limit  $D_L = t \times S_b \times \sqrt{\frac{N+1}{N}}$  the terms have thier usual meaning :

$$t = \frac{(\bar{x} - \mu) \times \sqrt{N}}{\text{Std. dev. (s)}}; \quad t = \frac{r(n-2)^{\frac{1}{2}}}{(1-r^2)^{\frac{1}{2}}}$$

*t* = Students *t*-value and *r* = correlation coefficient and

Youden's method  $D_L = \bar{x} \pm 3 \times \text{Std. dev. for blank } (S_b \text{ or } \sigma)$

### *Tolerance limit for diverse ions*

Interference studies were made with 4 ppm V(V) at 1.8M acid system, the tolerance limit being the amount causing a deviation of more than 0.005 in the absorbance (Table 1). The method appeared to have high selectivity for majority of cations and anions.

### *Selectivity*

The Table shows that a large excess of anions and sequestering agents e.g. citrate, oxalate, phosphate, EDTA have been tolerated upto the amount given in the Table ; Fe (III) interferes, but with fluoride as masking agent the tolerance limit increased to 25-fold excess. The selectivity and tolerance limits with Fe is also low in ternary extraction method and fluoride masking improved for moderate excess Fe. The tolerance ratio lies in between 1:10 and 1:50 in two of the ilmenite mineral (rock) and bauxite ore. The present method has been compared with other photometric methods and reported in Table 2.

### *Nature of the complex*

First a 1:2 complex is always formed in mibk in either case whether it is extracted from pH range or from acidity medium. The composition has been found to be fixed i.e. 1:2 in presence of excess amount of synergic thiocyanate ion. The molecular formula has been assigned to be  $\text{VO(OH) (CHA)}_2$  and  $\text{VO(CHA)}_2 \text{SCN}$  for binary and mixed-ligand chelate, respectively, by continuous variation, mole-ratio<sup>11</sup> and Hiskey-Meloche's methods<sup>12</sup>. Here, also, the ligands do not simply co-ordinate but a molecule with tautomeric forms, giving either keto or enol group, enhances the phase transfer processes with enhancement of polarization and rapid recovery *via* membrane transport through liquid interface. A very selective and rapid extraction takes place and this leads to highest sensitivity that can be achieved with hydroxamic acid<sup>13-18</sup>.

### *Application to real and environmental sample analysis (Steel, ore and rock)*

The ilmenite ores were processed before being used as the sample analysis and were passed through sieves for the bulk analyses. Their specifications were obtained. The method is highly reliable for all commercial low grade ores. Interfering ions were removed during the digestion with the reagents and the acids, and the filtration. The chief advantage is that the separations by extraction with recovery of vanadium from its ores are comparable for accurate and reproducible routine analyses. The method is simple and rapid. The results obtained after several runs were verified and compared with standard spectroscopic results or certified values. The results of the comparison give and reflect the method that is most rapid and has the highest accuracy. In conclusion, the aim of the work was to develop and



devise an analytical technique that was obviously simple and rapid, for application as a routine assay in geo-chemical mining and prospecting of rocks<sup>19</sup>.

Application of the technique to samples were tested using BAS 64B steel and two ilmenite samples collected from Putka Pahar, Madhya Pradesh (M.P.), India, and Tamil Nadu (Hornbendite rock), India, through the Geological Survey of India and IOL, Calcutta. The samples were finely ground (200 mesh) before direct analysis after separation. The methods were found to be excellent because of their high selectivity. The photometric procedures were found to be accurate, simple and high reproducible when fluoride was used for masking more than a 25-fold ratio of Fe and Ti present in excess. The proposed method had a comparable sensitivity and better selectivity than most of the reported spectrophotometric methods for vanadium. The reagent and the method is almost specific with masking agent. The samples were analysed by a spectroscopic method<sup>2</sup> and the result agreed well. The results are shown in Table 3.

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## Synthesis and characterization of silatranes containing heterocyclic moieties : Part III

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### Abstract

The nucleophilic substitution of 3-chloropropyltrimethoxysilane (1) with 1-hydroxymethyl-N-heterocycles such as 1-hydroxymethyl-3,5-dimethylpyrazole (2a), 1-hydroxymethylbenzotriazole (2b) and 1-hydroxymethylimidazole (2c) was carried out to form N-(het)oxamethylpropyltrimethoxy-silanes (3a-3c) in solution as intermediates. These were converted to their corresponding silatranes i.e., N-[3,5-dimethylpyrazolyl]oxamethylpropyl- (5a), N-[benzotriazolyl]oxamethylpropyl- (5b) and N-[imidazolyl]oxamethylpropylsilatranes (5c) by transesterification with triethanolamine (4). In an alternate method compound 1 was first converted to 3-chloropropylsilatrane (6) by reacting with compound 4 and then with 1-hydroxymethyl-N-heterocycles 2a-2c to obtain the same products 5a-5c in higher yields. Similarly, simple ester exchange of tetraethoxysilane (7) with compounds 2a-2c gave the corresponding N-(het)oxamethyltriethoxysilanes (8a-8c) which were easily converted to silatranes 9a-9c with compound 4. These silatranes have been characterized by elemental analyses, IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR.

(**Keywords** : heterocyclic substituted silatranes/transesterification).

### Introduction

Silatranes (2,8,9-trioxa-5-aza-1-silabicyclo[3,3,3]undecanes) are the most studied class of compounds with hypervalent silicon<sup>1-6</sup>. A number of silatranes have been shown to be highly toxic, while others are of potential pharmacological interest<sup>7-9</sup>.

Recently we have reported the heterocyclic substituted aminoalkyl silatranes<sup>10-12</sup>. In continuation of our work on heterocyclic substituted silatranes, we now report the synthesis of new class of N-(het)oxamethylpropylsilatranes and N-(het)oxamethylsilatranes, starting from 3-chloropropyltrimethoxysilane and tetraethoxysilane, respectively.

### Materials and Method

All the operations were carried out under Ar atmosphere. Xylene (LR), benzene (AR) and petroleum ether (AR, 40-60°C) were distilled and dried over sodium wire immediately

before use. Triethanolamine (LR) was vacuum distilled. KOH flakes (LR), pyridine (Qualigens, India), 3-chloropropyltrimethoxy silane (Fluka) and tetraethoxysilane (Fluka) were used as such. 3-Chloropropyl silatrane (6)<sup>13</sup>, 1-hydroxymethyl-3,5-dimethylpyrazole (2a)<sup>14</sup>, 1-hydroxymethyl benzotriazole (2b)<sup>15</sup> and 1-hydroxymethylimidazole (2c)<sup>11</sup> were prepared as described in literature.

Melting points taken on Toshniwal melting point apparatus are uncorrected. IR spectra were recorded on a Nicolet Magna 750 FTIR spectro photometer using KBr discs. <sup>1</sup>H and <sup>13</sup>C NMR were recorded in CDCl<sub>3</sub> on Jeol 90 FX and Bruker DPX 300 with tetramethylsilane as an internal standard. Chemical shifts are quoted in ppm downfield from TMS. C, H and N analyses were carried on elemental analyser system GmbH analyser: Vario EL.

#### *Synthesis of compounds 5a–5c : Typical Procedure*

*Method A* : 3-Chloropropyltrimethoxysilane (1) (7.95g, 40 mmol), 4 mL pyridine and 30 mL xylene were taken in a round bottom flask and to this 1-hydroxymethyl-3,5-dimethylpyrazole (2a) (5.04 g, 40 mmol) in 30 mL xylene was added dropwise during 20 min with stirring at room temperature in Ar atmosphere. After addition, the reaction mixture was refluxed for 21 h. Completion of the reaction was monitored by TLC (using EtOAc-pet.ether (40- 60°C) in 1:1 by volume) and IR. Pyridine hydrochloride was removed by filtration and the filtrate was concentrated in vacuum. It was taken in benzene and a calculated quantity of triethanolamine (4) was added to this in the presence of catalytic amount of KOH and then refluxed for 3–4 h. The usual work up yielded compound 5a. A similar procedure was followed for the preparation of compounds 5b and 5c.

*Method B* : Instead of compound 1, the starting material in this method is compound 6. Except the addition of triethanolamine (4) the rest of the procedure is similar as described in method A.

Compound **5a** was obtained as solid. IR (KBr disc, cm<sup>-1</sup>): 2931 vs (ν<sub>as</sub>CH<sub>2</sub>), 2875s (ν<sub>s</sub>CH<sub>2</sub>), 1129s, 1100s (νSi-O-C), 586m (νSi ←N), pyrazole moiety: 1055s, 1205m, 1550s and 1565w; <sup>1</sup>H NMR (δ ppm, CDCl<sub>3</sub>): 0.40 (t, 2H, SiCH<sub>2</sub>), 1.59 (m, 2H, C-CH<sub>2</sub>C), 2.11 (s, 3H, CH<sub>3</sub>), 2.20 (s, 3H, CH<sub>3</sub>), 2.69 (t, 6H, NCH<sub>2</sub>-atrane), 3.50(t, 2H, CH<sub>2</sub>O), 3.66 (t, 6H, OCH<sub>2</sub>-atrane), 5.54 (s, 2H, OCH<sub>2</sub>N), 5.76 (s, 1H, =CH); <sup>13</sup>C NMR (δ ppm, CDCl<sub>3</sub>): 10.70 and 12.90 (CH<sub>3</sub>), 15.15 (SiCH<sub>2</sub>), 22.32 (CCH<sub>2</sub>C), 50.20 (NCH<sub>2</sub>- atrane), 52.10 (CH<sub>2</sub>O), 57.52 (OCH<sub>2</sub>- atrane), 62.20 (OCH<sub>2</sub>N), 105.40 (C-4), 140.20 (C-3), 147.20 (C-5).

Compound **5b** was obtained as solid. IR (KBr disc, cm<sup>-1</sup>): 2929s (ν<sub>as</sub>CH<sub>2</sub>), 2871s (ν<sub>s</sub>CH<sub>2</sub>), 1127s, 1103s (νSi-O-C), 585m (νSi ←N), benzotriazole moiety: 1209s, 1565w, 1600m, 3005m and 3149m; <sup>1</sup>H NMR (δ ppm, CDCl<sub>3</sub>) : 0.48 (t, 2H, SiCH<sub>2</sub>), 1.88 (m, 2H,

C-CH<sub>2</sub>-C), 2.81 (s, 6H, NCH<sub>2</sub>-atrane), 3.61 (t, 2H, CH<sub>2</sub>O), 3.77 (t, 6H, OCH<sub>2</sub>-atrane), 5.65 (s, 2H, OCH<sub>2</sub>N), 6.20-7.91 (m, 4H, benzotriazole moiety); <sup>13</sup>C NMR (δ ppm, CDCl<sub>3</sub>): 14.18 (SiCH<sub>3</sub>), 28.78 (CCH<sub>2</sub>C), 48.22 (CH<sub>2</sub>O), 50.56 (NCH<sub>2</sub>-atrane), 57.16 (OCH<sub>2</sub>-atrane), 59.22 (OCH<sub>2</sub>N), benzotriazole moiety: 114.55 (C-7), 119.0 (C-4), 124.93 (C-5), 127.91 (C-6), 132.0 (C-7a), 145.10 (C-3a).

Compound **5c** was obtained as a hygroscopic solid. IR (KBr disc, cm<sup>-1</sup>): 2921s (ν<sub>as</sub>CH<sub>2</sub>), 2889s (ν<sub>s</sub>CH<sub>2</sub>), 1125s, 1100s (νSi-O-C), 584m (νSi←N), imidazole moiety: 1600w and 1662m.

#### *Synthesis of compounds 9a-9c : Typical Procedure*

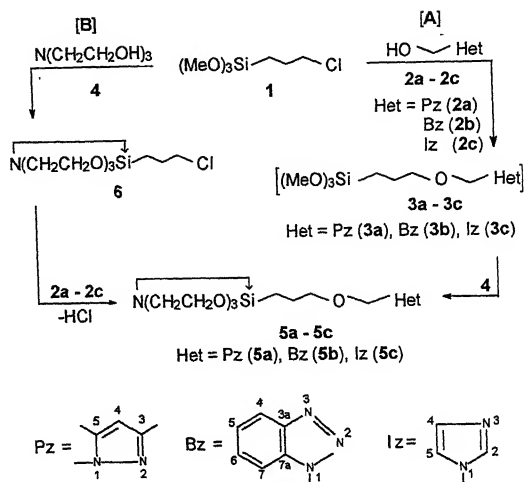
Tetraethoxysilane (**7**) (4.16 g, 20 mmol) and 0.5 g of titanium isopropoxide were taken in 30 ml xylene in a round bottom flask and to this 1-hydroxymethyl-3, 5-dimethylpyrazole (**2a**) (2.52 g, 20 mmol) in 20 ml xylene was added dropwise during 15 min with stirring at room temperature in Ar atmosphere. After addition the reaction mixture was refluxed for 12 h. Completion of the reaction was monitored by TLC (using EtOAc-pet.ether (40-60°C) in 3:1 by volume) and IR. The reaction mixture was filtered and the filtrate was concentrated in *vacuo* to obtain compound **8a** in solution. This was then converted to compound **9a** using same procedure as described for compounds **5a-5c**. A similar procedure was followed for the synthesis of compounds **9b** and **9c**. The compound **8b** could, however, be obtained in the solid state.

Compound **9a** was obtained as solid. IR (KBr disc, cm<sup>-1</sup>): 2932vs (ν<sub>as</sub>CH<sub>2</sub>), 2889s (ν<sub>s</sub>CH<sub>2</sub>), 1130s, 1105s (νSi-O-C), 586m (νSi←N), pyrazole moiety: 1038s, 1203 m, 1555s and 1569w; <sup>1</sup>H NMR (δ ppm, CDCl<sub>3</sub>): 2.13 (s, 3H, CH<sub>3</sub>), 2.27 (s, 3H, CH<sub>3</sub>), 2.77 (t, 6H, NCH<sub>2</sub>-atrane), 3.70 (t, 6H, OCH<sub>2</sub>-atrane), 4.55 (s, 2H, OCH<sub>2</sub>N), 5.79 (s, 1H, = CH); <sup>13</sup>C NMR (δ ppm, CDCl<sub>3</sub>): 11.40 and 12.69 (CH<sub>3</sub>), 51.20 (NCH<sub>2</sub>-atrane), 56.90 (OCH<sub>2</sub>N), 57.82 (OCH<sub>2</sub>-atrane), 102.82 (C-4), 140.0 (C-3), 146.30 (C-5).

Compound **8b** was obtained as solid. IR (KBr disc, cm<sup>-1</sup>): 2975w (ν<sub>as</sub>CH<sub>3</sub>), 2888s (ν<sub>s</sub>CH<sub>3</sub>), 2930vs (ν<sub>as</sub>CH<sub>2</sub>), 2840s (ν<sub>s</sub>CH<sub>2</sub>C), 1125s, 1098s (νSi-O-C), benzotriazole moiety: 1210s, 1577w, 1610m, 3003m and 3150m.

Compound **9b** was obtained as solid. IR (KBr disc, cm<sup>-1</sup>): 2919s (ν<sub>as</sub>CH<sub>2</sub>), 2880s (ν<sub>s</sub>CH<sub>2</sub>), 1130s, 1105s (νSi-O-C), 585m (νSi←N), benzotriazole moiety: 1209s, 1571w, 1611m, 3009m and 3149m; <sup>1</sup>H NMR (δ ppm, CDCl<sub>3</sub>): 2.72 (t, 6H, NCH<sub>2</sub>-atrane), 3.66 (t, 6H, OCH<sub>2</sub>-atrane), 4.87 (s, 2H, OCH<sub>2</sub>N), 6.28-8.05 (m, 4H, benzotriazole moiety), <sup>13</sup>C NMR (δ ppm, CDCl<sub>3</sub>): 51.22 (NCH<sub>2</sub>-atrane), 53.20 (CH<sub>2</sub>O), 57.72 (OCH<sub>2</sub>-atrane), 63.28 (OCH<sub>2</sub>N), benzotriazole moiety: 114.11 (C-7), 120.10 (C-4), 123.99 (C-5), 127.61 (C-6), 133.1 (C-7a), 144.0 (C-3a).

Compound **9c** was obtained as a hygroscopic solid. IR (KBr disc,  $\text{cm}^{-1}$ ) : 2928vs ( $\nu_{\text{as}}\text{CH}_2$ ), 2891s ( $\nu_{\text{s}}\text{CH}_2$ ), 1128s, 1103s ( $\nu_{\text{Si-O-C}}$ ), 586m ( $\nu_{\text{Si}\leftarrow\text{N}}$ ), imidazole moiety : 1605w and 1671m.

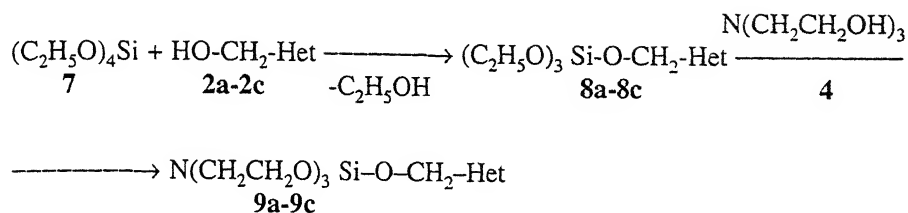


Scheme 1 – Synthesis of N-(het) oxamethylpropylsilatranes.

## Results and Discussion

We have developed two routes (Scheme 1) for the synthesis of the heterocyclic substituted silatranes **5a-5c**. By route [A], 3-chloropropyltrimethoxysilane (**1**) was first converted to heterocyclic substituted silanes **3a-3c** by its reactions with 1-hydroxymethyl-3,5-dimethylpyrazole (**2a**), 1-hydroxymethyl-1H-benzotriazole (**2b**) and 1-hydroxymethyl-1H-imidazole (**2c**), respectively, in the presence of pyridine as an acid abstractor. The reaction time was around 20-25 h in all the cases. The compounds **3a-3c** were, however, not isolated and one-pot reaction was carried to obtain their corresponding silatranes via transesterification reaction with triethanolamine (**4**). Compounds **5a** and **5b** were obtained as stable solids while compound **5c** was hygroscopic in nature. In an alternate route [B], the reaction of 3-chloropropylsilatrane (**6**) (obtained by the reaction between compound **1** and triethanolamine (**4**)) with 1-hydroxymethyl-N-heterocycles **2a-2c** yielded the same heterocyclic substituted silatranes **5a-5c** which were identical in all respects to the ones obtained by route [A].

Similarly, the tetraethoxysilane (**7**) was reacted with compounds **2a-2c** in the presence of titanium isopropoxide as a catalyst yielding the corresponding heterocyclic substituted silanes **8a-8c** according to the following scheme.



In all the cases the reaction time was around 12-19 h. The transesterification of compounds **8a** and **8c** *in situ* with triethanolamine (**4**) yielded compounds **9a** and **9c**. Compound **8b** could, however, be isolated and converted to compound **9b**. Compounds **9a** and **9b** were obtained as stable solids while the compound **9c** was hygroscopic in nature.

All the compounds were characterized by elemental analysis (Table 1), IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of compounds **5c** and **9c** could not be recorded due to their low solubility in common organic solvents. However, IR spectra did show characteristics of the proposed compounds.

**Infrared Spectra :** In the IR spectra of compounds **5a-5c**, the absence of C-Cl and O-H frequencies at 620 and 3150-3300  $\text{cm}^{-1}$ , respectively, completely rules out the presence of the reactants. They do show frequencies corresponding to the heterocyclic moieties<sup>10,11</sup> (as given under experimental section). Two strong bands in the region 1125-1130 and 1100-1107  $\text{cm}^{-1}$  in compounds **5a-5c** and **9a-9c** can be attributed to  $\nu\text{Si-O-C}$  absorption and the band in the region 584-586  $\text{cm}^{-1}$  to  $\nu\text{Si-N}$  absorption indicating the coordination of the nitrogen atom to silicon in the bicyclic compounds<sup>8</sup>.

**$^1\text{H}$  NMR spectra :** The  $^1\text{H}$  NMR spectra of all these compounds are as expected. The  $\text{NCH}_2$  and  $\text{OCH}_2$  protons of the atrane fragment of the compounds **5a**, **5b**, **9a** and **9b** appeared as triplets in the region between 2.69- 2.81 and 3.66-3.77 ppm, respectively. The  $\text{OCH}_2\text{C}$  protons of compounds **5a** and **5b** (at 3.50 and 3.61 ppm, respectively) appear at somewhat downfield as compared with  $\text{ClCH}_2\text{C}$  protons (3.40 ppm) in the parent compounds **1** and **6** due to replacement of Cl by more electronegative O. The  $\text{OCH}_2\text{N}$  protons of compounds **5a** and **5b** appeared as singlets at  $\delta$  5.54 and 5.65 ppm, respectively. The methylene ( $\text{OCH}_2\text{N}$ ) protons for compound **5a** appeared at a lower field as compared with the compound **2a** (the proton signals of compound **2a** appeared at  $\delta$  2.19 (s, 3H,  $\text{CH}_3$ ), 2.32 (s, 3H,  $\text{CH}_3$ ), 5.39 (s, 2H,  $\text{OCH}_2\text{N}$ ) and 5.82 (s, 1H,  $=\text{CH}$ ) ppm<sup>10</sup>), and those of compound **5b** appeared at higher field as compared to the compound **2b** (the  $\text{OCH}_2\text{N}$  proton signal of compound **2b** appeared at  $\delta$  6.12 (s, 2H,  $\text{OCH}_2\text{N}$ ) ppm<sup>16,17</sup>). However, the methylene ( $\text{OCH}_2\text{N}$ ) protons for compounds **9a** and **9b** appeared at higher field as compared to compounds **2a** and **2b**.

Table 1 – Physical and analytical data of heterocyclic substituted silane/silatrane.

Compd.	Empirical formula (Formula wt.)	M.p. (°C)	Yield (%)	Found (Calc.) %			
				C	H	N	Si
5a	C <sub>15</sub> H <sub>27</sub> N <sub>3</sub> O <sub>4</sub> Si (341.49)	122-124	60	52.10 (52.75)	7.45 (7.96)	12.71 (12.30)	8.35 (8.22)
5b	C <sub>16</sub> H <sub>24</sub> N <sub>4</sub> O <sub>4</sub> Si (364.48)	109-111	66	53.41 (52.72)	7.10 (6.63)	14.98 (15.37)	8.11 (7.70)
5c	C <sub>13</sub> H <sub>23</sub> N <sub>3</sub> O <sub>4</sub> Si (313.43)	–	60	48.98 (49.82)	7.56 (7.40)	13.80 (13.41)	9.13 (8.95)
8b	C <sub>13</sub> H <sub>21</sub> N <sub>3</sub> O <sub>4</sub> Si (311.42)	150-152 <sup>d</sup>	52	50.44 (50.13)	6.98 (6.79)	13.65 (13.49)	8.75 (9.01)
9a	C <sub>12</sub> H <sub>21</sub> N <sub>3</sub> O <sub>4</sub> Si (299.41)	200-202 <sup>d</sup>	50	47.97 (48.13)	7.45 (7.06)	14.27 (14.03)	8.98 (9.38)
9b	C <sub>13</sub> H <sub>18</sub> N <sub>4</sub> O <sub>4</sub> Si (322.40)	78-80	50	48.65 (48.43)	6.03 (5.62)	17.56 (17.37)	9.05 (8.71)
9c	C <sub>10</sub> H <sub>17</sub> N <sub>3</sub> O <sub>4</sub> Si (217.35)	–	55	44.55 (44.26)	6.72 (6.32)	15.20 (15.49)	10.61 (10.34)

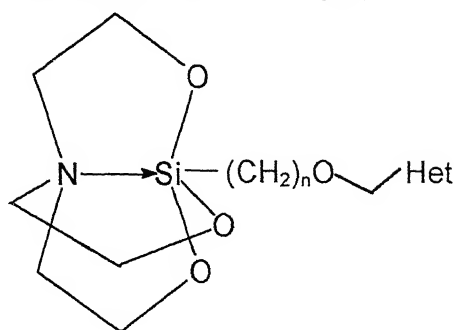
<sup>d</sup>decomposition point.

The down-field shift of atrane NCH<sub>2</sub> protons of the heterocyclic substituted compound as compared with that of triethanolamine (which appears at 2.61 ppm<sup>1</sup>) confirms the coordination of N with Si atom.

<sup>13</sup>C NMR spectra : In the <sup>13</sup>C NMR spectra, the signals of CH<sub>3</sub>, OCH<sub>2</sub>N, C-4, C-3 and C-5 of compounds **5a** and **9a** appeared in the region δ 10.70-11.40, 12.69-12.90, 56.90-62.20, 102.82-105.40, 140.0-140.20 and 146.30-147.20 ppm, respectively. (The <sup>13</sup>C signals of compound **2a** appeared at δ 10.53 (CH<sub>3</sub>), 12.97 (CH<sub>3</sub>), 69.99 (OCH<sub>2</sub>N), 106.10 (C-4), 139.97 (C-3), 149.42 (C-5) ppm,<sup>10</sup>). In case of compound **9a**, the OCH<sub>2</sub>N-N appeared at higher field (56.90 ppm) as compared with the compound **5a** where it appeared at δ 62.20 ppm. It may be due to the fact that the electron density at Si-O-C in case of compound **9a** is higher as compared with the **5a** where silicon and oxygen atom in Si-O is separated by propyl group.

Having observed the coordination of N (of the triethanolamino moiety) with the Si atom from IR and NMR spectral data, a proposed structure of silatrane is shown in Fig.1.





$n = 3$  for compounds **5a-5c**,  $n = 0$  for compounds **9a-9c**

Fig. 1

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## Stability of a stratified partially ionized plasma

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### Abstract

The effects of Hall currents and magnetic resistivity on the stratified layer of a viscous finitely conducting incompressible partially ionized plasma in a horizontal magnetic field has been investigated. It is shown that the system is characterized by a variational principle and by making use of it, solution have been obtained for a semi-infinite plasma in which density varies exponentially along the vertical. The dispersion relation has been derived and solved numerically. It is found that collisions with neutrals and viscosity have stabilizing influence while finite conductivity and Hall currents have destabilizing influence on the growth rate of the unstable mode of disturbance.

(Keywords : stratified plasma/hydromagnetic stability/viscosity/finite resistivity)

### Introduction

The hydromagnetic stability of a magnetized plasma of varying density is of considerable importance in several astrophysical situations, e.g. in theories of sunspot magnetic fields, heating of a solar corona, stability of stellar atmospheres in magnetic fields and in spiral arms of the galaxy in regard to star formation. Several authors<sup>1-8</sup> have studied the effects of Hall currents on the problem of Rayleigh-Taylor instability in hydromagnetics. This problem has been studied by several authors under varying physical conditions and a comprehensive account of the investigation of this problem as also of other stability studies has been given by Chandrasekhar<sup>9</sup> and Drazin and Reid<sup>10</sup>. In cosmic physics there are several situations such as chromospheres, solar photosphere and in cool interstellar clouds where the plasma are frequently not fully ionized but may instead be partially ionized so that the interaction between the ionised fluid and the neutral gas becomes important. Alfven<sup>11</sup> has pointed out the importance of such collisions between ionized fluid and neutral gas on the ionization rate in these regions. Maheswari and Bhatia<sup>12</sup> have studied the instability of a stratified partially ionized plasma permeated by uniform horizontal magnetic field along the x-axis. More recently Gupta and Bhatia<sup>13</sup> studied the instability of partially ionized superposed plasmas in a uniform two dimensional horizontal magnetic field.

The authors, Khan and Bhatia<sup>14</sup>, have studied the stability of a viscous Hall incompressible stratified ideally conducting plasma in a 2-D horizontal magnetic field.

Since magnetic resistivity is zero equally important an astrophysical situation. We have examined here the stability of a viscous Hall stratified plasma in the combined presence of effects of Hall currents and magnetic resistivity.

### Perturbation Equations

We consider the motion of an incompressible, viscous, finitely conducting hydromagnetic fluid of density  $\rho$  permeated with neutrals of density  $\rho_d$  ( $\rho \gg \rho_d$ ) which is in equilibrium under the action of a two dimensional uniform horizontal magnetic field  $\vec{H} = (H_x, H_y, 0)$  and gravitational field  $\vec{g} = (0, 0, -g)$  pointing downward. It is assumed that the two components of the partially ionized plasma (the ionized fluid and the neutral gas) behave as continuums and their steady state velocities are equal. Furthermore, we assume that the magnetic field interacts only with the ionized component of the plasma and that the frictional force of the neutral gas on the ionized fluid is of the same order as the pressure gradient of the ionized fluid. The pressure gradient of the neutrals is much less than the frictional force of the ionized atoms on the neutrals, and gravity has insignificant effect on the dynamics of the neutral gas. The investigation of the instability problem is quite complex. Consequently we have carried out here an investigation of the instability problem using above stated simple model of the partially ionized plasma. The problem is then tractable mathematically and it is hoped that the essential features of the problem are revealed by the model considered.

Under the forgoing assumptions the linearized perturbation equations appropriate to the flow of the mixture of hydromagnetic fluid and a neutral gas are,

$$\rho \frac{\partial \vec{u}}{\partial t} = -\nabla \delta p + \vec{g} \delta \rho + (\nabla \times \vec{h}) \times \vec{H} + \mu \nabla^2 \vec{u} + (\nabla \vec{u}) \cdot \nabla \mu + (\nabla \mu) \cdot \nabla \vec{u} + \rho_d v_c (\vec{u}_d - \vec{u}) \quad (1)$$

$$\frac{\partial \vec{u}_d}{\partial t} = -v_c (\vec{u}_d - \vec{u}) \quad (2)$$

$$\frac{\partial \vec{h}}{\partial t} = \nabla \times (\vec{u} \times \vec{H}) + \eta \nabla^2 \vec{h} - \frac{1}{Ne} \nabla \times [(\nabla \times \vec{h}) \times \vec{H}] \quad (3)$$

$$\frac{\partial}{\partial t} \delta \rho + (\vec{u} \cdot \nabla) \rho = 0 \quad (4)$$

$$\nabla \cdot \vec{u} = 0, \quad \text{and} \quad \nabla \cdot \vec{h} = 0 \quad (5)$$

where  $\vec{u}(u, v, w)$ ,  $\vec{h}(h_x, h_y, h_z)$ ,  $\delta\rho$ ,  $\delta p$  are respectively the perturbations in velocity, magnetic field  $\vec{H}$ , density  $\rho$  and pressure  $p$  of the ionized plasma, while  $\rho_d$  and  $\vec{u}_d$  denote the corresponding quantities for the neutral gas.

In the above equation,  $\mu$  is the coefficient of viscosity,  $\eta$  is magnetic resistivity.  $v_c$  is the collision frequency between the two components of the plasma while  $e$  and  $N$  are the charge and number densities of the particle.

Analysing the disturbance into normal modes we assume that the perturbed quantities have the dependence on the space coordinates  $(x, y, z)$  and time  $t$  of the form

$$F(z) \exp(ik_x x + ik_y y + nt) \quad (6)$$

where  $F(z)$  is some function of  $z$ ,  $k_x$  and  $k_y$  ( $k^2 = k_x^2 + k_y^2$ ) are the horizontal wave numbers and  $n$  (may be complex) denote the rate at which a system departs away from equilibrium.

On using (6) in eqn. (1) – (5) and on writing

$$n_c = n \left( 1 + \frac{\alpha v_c}{n + v_c} \right), \quad \alpha = \frac{\rho_d}{\rho}, \quad D = \frac{d}{dz} \quad (7)$$

Eliminating some of the variables from these equations we obtain a set of four equations in four variables  $w$ ,  $h_z$ ,  $\zeta$  and  $\xi$ .

$$\begin{aligned} n_c \left[ \rho k^2 w - D(\rho Dw) \right] - \frac{gk^2}{n} (D\rho) w + (ik_x H_x + ik_y H_y) (D^2 - k^2) h_z \\ + \mu (D^2 - k^2)^2 w + 2(D\mu) (D^2 - k^2) Dw + (D^2 + k^2) (D^2 \mu) w = 0 \end{aligned} \quad (8)$$

$$\left[ n - \eta (D^2 - k^2) \right] h_z + \frac{1}{Ne} (ik_x H_x + ik_y H_y) \xi = (ik_x H_x + ik_y H_y) w \quad (9)$$

$$\begin{aligned} \left[ n - \eta (D^2 - k^2) \right] \xi - \frac{1}{Ne} (ik_x H_x + ik_y H_y) (D^2 - k^2) h_z \\ = (ik_x H_x + ik_y H_y) \zeta \end{aligned} \quad (10)$$

$$n_c \rho \zeta = (ik_x H_x + ik_y H_y) \xi + (D\mu) (D\zeta) + \mu (D^2 - k^2) \zeta \quad (11)$$

where

$$\zeta = ik_x v - ik_y u, \quad \xi = ik_x h_y - ik_y h_x \quad (12)$$

are respectively the vertical components of the vectors  $\vec{u}$  and  $\vec{h}$ .

#### *Boundary Conditions*

We have thus a set of four equations in four variables  $w$ ,  $h_z$ ,  $\zeta$  and  $\xi$  which are to be solved subject to the appropriate boundary conditions, depending upon whether the bounding surface are free or rigid.

In the present paper we assume that the plasma is confined between two rigid planes at  $z = 0$  and  $z = d$  which are both assumed to be ideal conductors. The normal component of the velocity must vanish at these boundaries, we must therefore have,

$$w = 0 \quad \text{at} \quad z = 0 \quad \text{and} \quad z = d \quad (13)$$

If the fluid terminates at a rigid boundary  $\vec{u}$  must vanish, therefore

$$\zeta = 0, \quad h_z = 0 \text{ at a rigid boundary} \quad (14)$$

Finally eqn. (11) gives on using (13) and (14)

$$\xi = 0 \quad \text{at} \quad z = 0 \quad \text{and} \quad z = d \quad (15)$$

### Variational Principle

Let us suppose that the solution  $h_i$ ,  $w_i$ ,  $\zeta_i$  and  $\xi_i$  belonging to the characteristic value  $n_i$  and  $h_j$ ,  $w_j$ ,  $\zeta_j$  and  $\xi_j$  belonging to  $n_j$  where we have dropped the suffix  $z$  on  $h$  for simplicity.

Multiplying eqn. (8) for  $i$  by  $w_j$  and integrating across the vertical extent  $L$  of the plasma, using the boundary conditions and setting  $i = j$  in the integrals we get finally

$$\begin{aligned}
 & n_c \left[ \int_L \rho \left[ k^2 w^2 + (Dw)^2 \right] dz - \int_L \rho \zeta^2 dz \right] - \frac{gk^2}{n} \int_L (D\rho) w^2 dz \\
 & + n \left[ \int_L \xi^2 dz - \int_L \left[ (Dh)^2 + k^2 h^2 \right] dz \right] + \eta \left[ \int_L \left[ (D\xi)^2 + k^2 \xi^2 \right] dz \right. \\
 & \left. - \int_L \left[ (D^2 h)^2 + 2k^2 (Dh)^2 + k^4 h^2 \right] dz \right] + \int_L \mu \left[ (D^2 + k^2)^2 w^2 + 4k^2 (Dw)^2 \right] dz \\
 & - \int_L \mu \left[ (D\zeta)^2 + k^2 \zeta^2 \right] dz = 0
 \end{aligned} \tag{16}$$

Considering a variation  $\delta n$  in  $n$  consequent to the variations  $\delta w$ ,  $\delta h$ ,  $\delta \zeta$  and  $\delta \xi$  related to it through perturbation form of eqn. (9), (10) and (11) in  $w$ ,  $h$ ,  $\zeta$  and  $\xi$  respectively compatible with the boundary conditions and proceeding along the usual lines we can show that to first order  $\delta n = 0$ .

### Stratified Layer of a Composite Plasma

We now use of the existence of the variational principle to obtain the solution of the problem of stability of a semi-infinite plasma in which the density is continuously stratified exponentially along the vertical i.e.

$$\rho(z) = \rho_0 \exp(\beta z) \tag{17}$$

where  $\rho_0$  and  $\beta$  are constant. It is assumed that the plasma is confined between two surfaces which are separated by the distance of  $d$  units. The plasma is also assumed to be extending infinitely along both  $x$  and  $y$  directions.

Furthermore, for mathematical simplicity, we make assumption that,

$$|\beta d| \ll 1 \quad (18)$$

Appropriate to boundary conditions, let us assume the following trial solutions for  $w$ ,  $h$ ,  $\zeta$ , and  $\xi$

$$\begin{aligned} w(z) &= A_1 \sin lz, & h(z) &= A_2 \sin lz \\ \zeta(z) &= A_3 \sin lz, & \xi(z) &= A_4 \sin lz \end{aligned} \quad (19)$$

where  $A_1$ ,  $A_2$ ,  $A_3$  and  $A_4$  are constants and  $l = \frac{\pi s}{d}$ ,  $s$  being an integer. Substituting these trial solutions in eqn. (16) and (19) and eliminating the constants  $A_1$ ,  $A_2$ ,  $A_3$  and  $A_4$  by using (9) – (11) we finally obtain a dispersion relation as

$$\begin{aligned} nn_c - \frac{g\beta k^2}{l^2 + k^2} &= n v_0 (l^2 + k^2) + n(\vec{k} \cdot \vec{V})^2 \\ \cdot \left[ n + \eta (l^2 + k^2) + \frac{\left( \frac{\vec{k} \cdot \vec{H}}{Ne} \right)^2 (l^2 + k^2) \{n_c + v_0 (l^2 + k^2)\}}{(\vec{k} \cdot \vec{V})^2 + \{n + \eta (l^2 + k^2)\} \{n_c + v_0 (l^2 + k^2)\}} \right] &= 0 \end{aligned} \quad (20)$$

$$\text{where } \vec{k} \cdot \vec{V} = \frac{k_x H_x + k_y H_y}{\sqrt{f_0}} \quad \text{and} \quad \frac{\vec{k} \cdot \vec{H}}{Ne} = \frac{k_x H_x + k_y H_y}{Ne}$$

On writing



$$Y = \frac{n}{l}, \quad S = \frac{g\beta}{l^2}, \quad C = \frac{v_c}{l}, \quad N = v_0 l, \quad M = \eta l$$

$$L_1 = \frac{H_x l}{Ne}, \quad L_2 = \frac{H_y l}{Ne}, \quad V_1 = \frac{H_x}{\sqrt{\rho_0}}, \quad V_2 = \frac{H_y}{\sqrt{\rho_0}} \quad (21)$$

We obtain the non-dimensional form of the dispersion relation as

$$\begin{aligned} & Y^7 + 2Y^6 \left[ C(1+\alpha) + (1+x^2)(M+N) \right] + Y^5 \left[ N(1+x^2)^2(N+4M) \right. \\ & + C(1+\alpha) \{ 4M(1+x^2) + C(1+\alpha) \} + (1+x^2) \{ 2NC(2+\alpha) + (M^2(1+x^2) \\ & + x^2(L_1 \cos\theta + L_2 \sin\theta)^2) \} - \frac{Sx^2}{1+x^2} + 2x^2(V_1 \cos\theta + V_2 \sin\theta)^2 \Big] \\ & + Y^4 \left[ 2N(1+x^2) \{ x^2(V_1 \cos\theta + V_2 \sin\theta)^2 + NC + NM(1+x^2)^2 \} \right. \\ & + \{ x^2(L_1 \cos\theta + L_2 \sin\theta)^2 + M^2(1+x^2) \} \{ N(1+x^2)^2 \\ & + 2C(1+\alpha)(1+x^2) - Sx^2 \} + (1+x^2) \{ 2Mx^2(V_1 \cos\theta + V_2 \sin\theta)^2 \\ & + N(1+x^2)(M^2 + x^2(L_1 \cos\theta + L_2 \sin\theta)^2) \} - 2MSx^2 \\ & + C^2(1+x^2)(1+\alpha) \{ M(1+\alpha) + 2N \} + C(2+\alpha) \{ 2x^2(V_1 \cos\theta + V_2 \sin\theta)^2 \\ & + 4MN(1+x^2)^2 - \frac{Sx^2}{1+x^2} \} \Big] + \\ & + Y^3 \left[ \{ x^2(L_1 \cos\theta + L_2 \sin\theta)^2 + M^2(1+x^2) \} \{ C^2(1+\alpha)^2(1+x^2) - Sx^2 \right. \end{aligned}$$

$$\begin{aligned}
& + C(2 + \alpha) (N(1 + x^2)^2 - Sx^2) + N^2(1 + x^2) \Big\} + C^2 N^2 (1 + x^2)^2 \\
& + C(2 + \alpha) \Big\{ (1 + x^2) (2Mx^2 (V_1 \cos\theta + V_2 \sin\theta)^2 + N(1 + x^2) (M^2 + \\
& + x^2 (L_1 \cos\theta + L_2 \sin\theta)^2) - 2MSx^2) \Big\} \\
& + C^2(1 + \alpha) \Big\{ 2x^2 (V_1 \cos\theta + V_2 \sin\theta)^2 + 4MN(1 + x^2)^2 - \frac{Sx^2}{1 + x^2} \Big\} \\
& + \Big\{ 2MN(1 + x^2) - x^2 (V_1 \cos\theta + V_2 \sin\theta)^2 \Big\} \Big\{ x^2 (V_1 \cos\theta + V_2 \sin\theta)^2 - \frac{Sx^2}{1 + x^2} \Big\} \\
& + 2C \Big\{ 2N(1 + x^2) (2MN(1 + x^2)^2 + x^2 (V_1 \cos\theta + V_2 \sin\theta)^2) - SNx^2 \Big\} \\
& + Y^2 \Big[ \Big\{ x^2 (L_1 \cos\theta + L_2 \sin\theta)^2 + M^2(1 + x^2) \Big\} \Big\{ C^2(1 + \alpha) (N(1 + x^2)^2 - Sx^2) \\
& - Sx^2 (Mx^2 (V_1 \cos\theta + V_2 \sin\theta)^2 + N(1 + x^2) + C(2 + \alpha)) + 2CN^2(1 + x^2)^3 \Big\} \\
& + 2C \Big\{ 2MN(1 + x^2) - x^2 (V_1 \cos\theta + V_2 \sin\theta)^2 \Big\} \Big\{ x^2 (V_1 \cos\theta + V_2 \sin\theta)^2 - \frac{Sx^2}{1 + x^2} \Big\} \\
& + C^2 N \Big\{ 2N(1 + x^2) (x^2 (V_1 \cos\theta + V_2 \sin\theta)^2 + MN(1 + x^2)^2) - Sx^2 \Big\} \Big] \\
& + Y \Big[ \Big\{ x^2 (L_1 \cos\theta + L_2 \sin\theta)^2 + M^2(1 + x^2) \Big\} \Big\{ C^2 N^2(1 + x^2)^3 \\
& - CSx^2 (C(1 + \alpha) + 2N(1 + x^2)) \Big\} - 2SCx^4 M (V_1 \cos\theta + V_2 \sin\theta)^2 \\
& + C \Big\{ x^2 (V_1 \cos\theta + V_2 \sin\theta)^2 - \frac{Sx^2}{1 + x^2} \Big\} \Big\{ 2MN(1 + x^2)^2
\end{aligned}$$

$$\begin{aligned}
& -x^2 (V_1 \cos\theta + V_2 \sin\theta)^2 \Big] - Sx^2 C^2 \left[ Mx^2 (V_1 \cos\theta + V_2 \sin\theta)^2 \right. \\
& \left. + N(1+x^2) \{x^2 (L_1 \cos\theta + L_2 \sin\theta)^2 + M^2(1+x^2)\} \right] = 0
\end{aligned} \quad (22)$$

where  $\theta$  is the angle between  $\vec{k}$  and  $H_x$  and  $V_1$  and  $V_2$  are Alfven velocities while  $L_1$  and  $L_2$  are Hall currents in  $x$  and  $y$  directions respectively.

When  $M = 0$  i.e.  $\eta = 0$ , we recover the dispersion relation obtained earlier by Khan and Bhatia<sup>14</sup>.

Table 1 – Values of growth rate (positive real value of  $Y$ ) against wave number  $x$  for  $C = 0.1, 0.2, 0.3$  and  $N = 0.1, 0.2, 0.3$  when  $M = 1.0$ ,  $V_1 = V_2 = 0.5$ ,  $S = 20.0$ ,  $L_1 = L_2 = 1.0$  and  $\theta = 45^\circ$

$x$	Values of growth rate					
	$N = 1.0$			$C = 0.2$		
	$C = 0.1$	$C = 0.2$	$C = 0.3$	$N = 0.1$	$N = 0.2$	$N = 0.3$
0.0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1	0.1616	0.1657	0.1702	0.1657	0.0950	0.0658
0.2	0.4865	0.4829	0.4837	0.4829	0.2998	0.2171
0.3	0.8477	0.8430	0.8409	0.8430	0.5531	0.4072
0.4	1.1963	1.1932	1.1913	1.1932	0.8148	0.6097
0.5	1.5210	1.5191	1.5178	1.5191	1.0605	0.8031
0.6	1.8192	1.8177	1.8166	1.8177	1.2819	0.9772
0.7	2.0915	2.0898	2.0884	2.0898	1.4771	1.1289
0.8	2.3395	2.3370	2.3350	2.3370	1.6472	1.2590
0.9	2.5651	2.5614	2.5584	2.5614	1.7942	1.3693
1.0	2.7705	2.7652	2.7607	2.7652	1.9205	1.4622

### Discussion

(A) *Stable Stratification* ( $S < 0$ ) : Applying Hurwitz criterion to the case of  $S < 0$  we find that as all the terms of eqn. (22) are then positive, all the roots of  $Y$  are either real and

Table 2 – Values of growth rate (positive real value of  $Y$ ) against wave number  $x$  for  $L = 1.0, 2.0, 3.0$  and  $M = 1.0, 2.0, 3.0$  when  $N = 1.0, C = 0.2, V_1 = V_2 = 0.5, S = 20.0$ , and  $\theta = 45^\circ$

x	Values of growth rate					
	M = 1.0			L = 1.0		
	L = 1.0	L = 2.0	L = 3.0	M = 1.0	M = 2.0	M = 3.0
0.0	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
0.1	0.1657	0.1661	0.1668	0.1657	0.1704	0.1725
0.2	0.4829	0.4909	0.5017	0.4829	0.5187	0.5387
0.3	0.8430	0.8764	0.9182	0.8430	0.9345	0.9948
0.4	1.1932	1.2757	1.3732	1.1932	1.3486	1.4626
0.5	1.5191	1.6730	1.8464	1.5191	1.7354	1.9062
0.6	1.8177	2.0616	2.3241	1.8177	2.0896	2.3162
0.7	2.0898	2.4371	2.7960	2.0898	2.4116	2.6918
0.8	2.3370	2.7966	3.2544	2.3370	2.7040	3.0352
0.9	2.5614	3.1377	3.6931	2.5614	2.9693	3.3489
1.0	2.7652	3.4586	4.1073	2.7652	3.2100	3.6356

negative or there is one negative real root and the remaining roots are complex with negative real parts, implying thereby stability in each case. Thus the system remains stable whether the effects of Hall currents and viscosity are included separately or jointly.

(B) *Unstable Stratification* ( $S > 0$ ) : The dispersion relation (22), being a polynomial of seventh degree, must possess at least one real root the sign of which is opposite to that of the last term. Since the last term is always negative for  $S > 0$ , eqn. (22), therefore possesses at least one positive real root for all wave number  $x$ , consequently the system is unstable for all wave numbers. We thus see that the system is unstable at all wave numbers in the presence of viscosity and Hall currents.

The dispersion relation (22) is quite complex. In order to study the influence of various physical effects on the growth rate of unstable modes, numerical calculations of the dispersion relation (22) were performed to locate the roots of  $Y$  against  $x$  for several values of the parameters.

These calculations are presented in Tables (1 & 2) where we have plotted the growth rate  $Y$  (positive real part) against wave number  $x$  for different values of the parameters characterizing, neutral gas friction, viscosity, finite conductivity and Hall current taking  $\alpha=0.2$ ,  $V_1 = V_2 = 0.5$ ,  $S = 0$  and  $\theta = 45^\circ$ .

It is clearly seen from Table 1 that growth rate  $Y$  decreases as  $C$  (collisions with neutrals) increases for the same  $x$ , showing thereby stabilizing influence of neutral gas friction. From Table 1 it is seen that as  $N$  (viscosity) increases,  $Y$  (growth rate) decreases for the same  $x$  showing stabilizing character of viscosity. From Table 2 it is seen that as  $M$  (finite conductivity) increases,  $Y$  (growth rate) increases for the same  $x$  showing destabilizing character of finite conductivity. It is also seen from Table 2 that as  $L$  (Hall currents) increases,  $Y$  (growth rate) increases for the same  $x$  showing destabilizing character of Hall currents. These results are in agreement with earlier observations.

We may thus conclude that collision with neutrals and viscosity have stabilizing influence while finite conductivity and Hall currents have destabilizing influence on the Rayleigh Taylor instability of a partially ionized stratified plasma in a two dimensional uniform horizontal magnetic field.

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## Boundary value problems of infinite plate weakened by a circular hole

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### Abstract

Boundary value problems (Cauchy methods) are used to obtain an exact and closed expression for the stresses in the first and second boundary value problems of infinite plate weakened by a circular hole. The plate considered is conformally mapped on the domain outside the unit circle. The work of many previous authors, in this domain are considered as special cases of this problem. Some interesting cases when the shape of the hole takes other shapes are included as special cases.

### Introduction

Boundary value problems for isotropic homogeneous perforated infinite plates have been studied by several authors<sup>1,2,3</sup>. Some authors<sup>1,2</sup> used Laurant's theorem to express the potential as a power series. Others<sup>3-5</sup> used complex variable method of integral. Muskhelishvili<sup>5</sup> proved that the first and second fundamental plane theory of elasticity, are equivalent to finding two analytic functions of one complex argument  $z = x + iy$ , satisfying conditions

$$k \overline{\Phi_1(t)} - i \overline{\Phi_1'(t)} - \overline{\Psi_1(t)} = f(t) \quad (1)$$

$f(t)$  is a given function of stresses, for the first boundary value problem,  $\frac{+3\mu}{+ \mu} > 1, f = 2\mu g$  for the second boundary value problem and  $t$  denotes point on the boundary. Also, in the book of Muskhelishvili<sup>5</sup>, we find, for the stress components  $\tau_{xx}, \tau_{xy}, \tau_{yy}$ , that :

$$\tau_{xx} + \tau_{yy} = 4 \operatorname{Re} \phi_1'(z),$$

$$\tau_{yy} - \tau_{xx} + 2i\tau_{xy} = 2 [\overline{z}\phi_1''(z) + \psi_1'(z)]$$

and for the components of the displacement  $u, v$ ; that

$$2\mu(u + iv) = \kappa\phi_1(z) - z\overline{\phi_1'(z)} + \overline{\psi_1(z)}$$

In terms of rational mapping function  $z = cw(\xi)$ ,  $c > 0$ ,  $w'(\xi) \neq 0$  or  $\infty$  for  $|\xi| > 1$ , and in the absence of body forces, the Gaurast's functions  $\phi_1(z)$  and  $\psi_1(z)$  take the form

$$\phi_1(z) = \frac{X + iY}{2\pi(1 + \kappa)} \ln \xi + c\Gamma\xi + \phi(\xi) \quad (2)$$

$$\psi_1(z) = \frac{\kappa(X - iY)}{2\pi(1 + \kappa)} \ln \xi + c\Gamma^*\xi + \psi(\xi).$$

Here  $X, Y$  are the components of the resultant vector of all external forces, acting on the boundary  $\Gamma, \Gamma^*$  are constants, generally the complex functions  $\phi(\xi), \psi(\xi)$  are single valued analytic within the region of the plate and bounded at infinity.

In this work, we use the complex variable method to derive an exact expression for Gaurast's functions for the first and the second fundamental problems of the infinite plate weakened by a curvilinear hole  $C$  conformally mapped on the domain outside the unit circle  $\gamma$ , using the rational mapping

$$z = cw(\xi) = c \frac{\xi + m_1\xi^{-1} + m_2\xi^{-2} + m_3\xi^{-3}}{1 - n\xi^{-1}} \quad (c > 0) \quad (3)$$

where  $m_1, m_2, m_3, n$ , are real parameters subject to the condition  $z'(\xi)$  does not vanish or become infinite outside  $\gamma$ . Some applications of the problem on these domains are investigated, the interesting cases when the shape of the hole is a circle, an ellipse, a triangle, a square, a crescent or a cut having the shape of a circular arc are included as special cases. Several previously known solutions appear as special cases of this work. The boundaries of the holes corresponding to certain combinations of the parameters  $m_1, m_2, m_3, n$  are sketched in Fig. (1&2). In Fig. 1 two holes are sketched for two different values of  $n$  ( $n = -1/2, n = -1/3$ ) and the same values of  $m_1 = m_2 = m_3 = 0$ . In Fig. 2, two holes are sketched, the first one with  $m_1 = 0.7, m_2 = m_3 = 0, n = 0.1$  and the second hole with  $m_1 = 0.31, m_2 = m_3 = 0, n = 0.4$ .

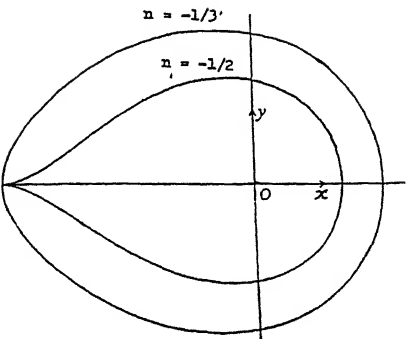


Fig. 1

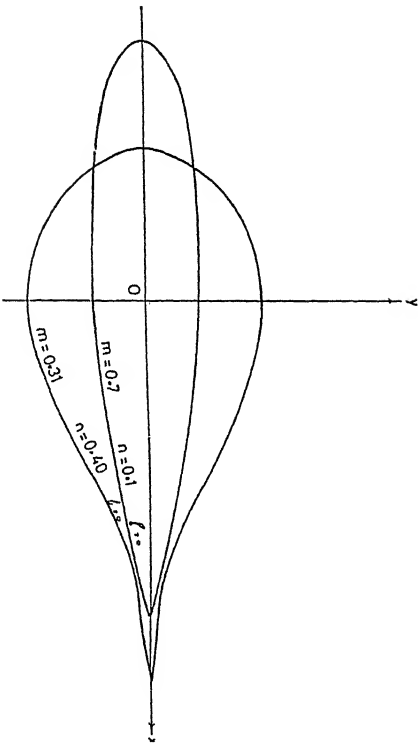


Fig. 2



### Gaurasts Function

Consider the function

$$\beta(\xi) = \frac{w(\xi^{-1})}{w'(\xi)} - \alpha(\xi^{-1}) \quad (4)$$

where

$$\alpha(\xi) = \frac{m_3 + m_2\xi + h\xi^2}{\xi^2(\xi - n)}$$

and

$$h = \frac{(1 + m_3)m_1 + m_1m_2n + C_1n^2 + m_2n^2 + C_2n^4 + n^6}{1 - (2 + m_1)n^2 - 2m_2n^3 - 3m_3n^4 + m_2n^5 + 2m_3n^6},$$

$$C_1 = 1 - 2m_1 + 2m_2^2 + 3m_3^2 + m_3, \quad C_2 = -2 + m_1 - m_2^2 + 2m_3^2.$$

$\beta(\xi)$  is regular function of  $|\xi| > 1$ . Using (2), and with the aids of (4), the boundary conditons (1) take the following form

$$\kappa\phi(\sigma) - \alpha(\sigma)\overline{\phi'(\sigma)} - \overline{\psi_*(\sigma)} = f_*(\sigma) \quad (5)$$

where,

$$\psi_*(\xi) = \psi(\xi) + \beta(\xi)\phi'(\xi),$$

$$f_*(\xi) = F(\xi) - ck\Gamma\xi + c\overline{\Gamma^*}\xi^{-1} + N(\xi)\frac{w(\xi)}{w'(\xi^{-1})}$$

$$N(\xi) = c\Gamma - \frac{X - iY}{2\pi(1 + \kappa)}\xi,$$

and

$$F(\xi) = f(cw(\xi)).$$

The function  $F(\xi)$  must have values satisfying the Hölder condition. By the same procedure, mentioned in literature<sup>5,6</sup> multiplying both sides of (5) by  $\frac{1}{2\pi i (\sigma - \xi)}$ , then integrating with respect to  $\sigma$  on the unit circle  $\gamma$ , the complex function  $\phi(\xi)$  and  $\psi(\xi)$  take the form

$$-\kappa\phi(\xi) = A(\xi) - \frac{c\overline{\Gamma}}{\xi} + c \frac{(m_3 + m_2\xi)\Gamma}{\xi^2 (n - \xi)} + \frac{chb_0}{n - \xi}, \quad (6)$$

$$\begin{aligned} \psi(\xi) = & \frac{c\kappa\Gamma}{\xi} - \frac{w(\xi^{-1})}{w'(\xi)} \phi_*(\xi) + \frac{h\xi}{1 - n\xi} \phi_*(n^{-1}) + B(\xi) + B \\ & + \frac{\xi}{1 - n\xi} \left[ (m_2 n^{-1} + m_3 n^{-2}) \phi'(n^{-1}) - \xi^2 \overline{N(\xi)} \right] \\ & - \frac{2cn(m_2 + nm_3)b_0\xi}{\kappa(1 - n^2)^2(n - \xi)^2} \end{aligned} \quad (7)$$

where

$$\phi_*(\xi) = \phi'(\xi) + \overline{N(\xi)},$$

$$A(\xi) = \frac{1}{2\pi i} \sum_{\eta=0}^{\infty} \xi^{-\eta-1} \int_{\gamma} \sigma^{\eta} F(\sigma) d\sigma \quad |\xi| > 1,$$

$$B(\xi) = \frac{1}{2\pi i} \int_{\gamma} \frac{\overline{F(\sigma)}}{\sigma - \xi} d\sigma,$$

and

$$B = \frac{1}{2\pi i} \int_{\gamma} \frac{\overline{F(x\sigma)}}{\sigma} d\sigma$$

Also, the complex constant  $b_0$  takes the form

$$b_0 = b + N(n), \quad b = \frac{kE - \nu hE}{c(k^2 - h^2\nu^2)} \quad (8)$$

where

$$\nu = \frac{m_3 + nm_2 + n^2h}{(1 - n^2)^2} \quad (9)$$

and

$$\begin{aligned} E = (m_2 + nm_3 + n^2) \left[ -\frac{A'(n^{-1})}{n^2} + C\Gamma^* \right] + c\nu n(n^2 - 1)(m_2 + nm_3)\Gamma \\ + \nu \bar{N} [n(n^2 - 2)(m_2 + nm_3) + h]. \end{aligned} \quad (10)$$

### Special cases

The following are some special cases that can be derived from our work.

*Case one* : For  $m_3 = 0$ , the mapping function, equation (1), takes the form

$$z = c \frac{\xi + m_1\xi^{-1} + m_2\xi^{-2}}{1 - n\xi^{-1}},$$

and the potential functions  $\phi(\xi)$ ,  $\psi(\xi)$  are obtained directly from (6) and (7), the results agree with literature<sup>6</sup>.

*Case two* : For  $m_2 = 0$ , the rational mapping function takes the form

$$z = c \frac{\xi + m_1\xi^{-1} + m_3\xi^{-3}}{1 - n\xi^{-1}}$$

and the results of (6) and (7) are in the agreement with literature<sup>5</sup>.

*Case three* : For  $m_2 = 0$  and  $m_3 = 0$ , we have the mapping function

$$z = c \frac{\xi + m_1\xi^{-1}}{1 - n\xi^{-1}}$$

and the results are in the agreement with literature<sup>4,5</sup>.

*Case four* : For  $m_2 = 0$ ,  $m_3 = 0$ , and  $m_1 = -1$ , we have the rational mapping function

$$z = c \frac{\xi - \xi^{-1}}{1 - n\xi^{-1}},$$

where the boundary  $C$  degenerates into a circular cut (see literature<sup>4,5</sup>).

*Examples :*

1. For  $k = 1$ ,  $\Gamma = \frac{P}{4}$ ,  $\Gamma^* = -\frac{1}{2} P e^{-2i\theta}$  and,  $X = Y = f = 0$ , the problem reduces to the infinite plate weakened by the curvilinear hole  $C$  which is free from stresses. The plate stretched at infinity by the application of a uniform tensile stress of intensity  $P$  making an angle  $\theta$  with the  $X$ -axis. The two complex functions can be written as :

$$\phi(\xi) = \frac{cP}{2} e^{-2i\theta} \xi^{-1} + \frac{cP(m_3 + m_2\xi)}{4\xi^2(n - \xi)} + \frac{ch b_0}{n - \xi},$$

$$\begin{aligned} \psi(\xi) = & \frac{c\kappa P}{4\xi} - \frac{w(\xi^1)}{w'(\xi)} \phi^*(\xi) + \frac{h\xi}{1 - n\xi} \phi^*(n^{-1}) \\ & + \frac{\xi}{1 - n\xi} \left[ (m_2 n^{-1} + m_3 n^{-2}) \phi'(n^{-1}) - \frac{CP}{4} \xi^2 \right] \end{aligned}$$

$$- \frac{2cn(m_2 + nm_3)b_0\xi}{\kappa(1 - n^2)^2(n - \xi^2)}$$

where  $b_0$  is given by (8) – (10) with

$$A'(n^{-1}) = 0, \quad N = \bar{N} = \frac{cP}{4}, \quad \Gamma = \frac{P}{4}, \quad \Gamma^* = \frac{-1}{2} P e^{-2i\theta}.$$

2. For  $k = 1$ ,  $X = Y = \Gamma = \Gamma^* = 0$  and  $f = Pt$  where  $P$  is a real constant, the Gaurast's functions become

$$\phi(\xi) = \frac{P[(m_1 + n^2)\xi^2 + m_3(1 - \xi)]}{\xi^2(n - \xi)} + \frac{chb}{n - \xi} \quad (11)$$

$$\begin{aligned} \psi(\xi) = & -c P \xi^{-1} - \frac{w(\xi^{-1})}{w'(\xi)} \phi_*(\xi) + \frac{h\xi}{1-n\xi} \phi_*(n^{-1}) \\ & + \frac{\xi \phi'(n^{-1})}{1-n\xi} (m_2 n^{-1} + m_3 n^{-2}) - \frac{2c n (m_2 + n m_3) b \xi}{\kappa (1-n^2)^2 (n-\xi)^2} \end{aligned} \quad (12)$$

where

$$b = \frac{kE - \nu h \bar{E}}{c(k^2 - h^2 \nu^2)},$$

and

$$E = \frac{P(2m_1 + (2m_3 + 3m_1)n + 3m_3 n^2 + 3m_3 n^3 - 2n^4)(m_2 + n m_3 + n^2)}{(1-n^2)^2}$$

The problem reduces to a first fundamental problem of an infinite plate weakened by a curvilinear hole  $C$ , when the edge of the hole is subjected to a uniform pressure  $P$ . In terms of (11) and (12), let  $P = -iT$ , we have the first fundamental problem when the edge of the hole is subject to a uniform tangential stress  $T$ .

3. For  $\dot{\Gamma} = \Gamma^* = f = 0$ ,  $k = \kappa$ , we have

$$\phi(\xi) = -\frac{ch b_0}{\kappa(n-\xi)},$$

$$\begin{aligned} \psi(\xi) = & \frac{w'(\xi^{-1})}{w'(\xi)} \phi'(\xi) + \frac{h\xi}{1-n\xi} \phi_*(n^{-1}) + \frac{\xi}{1-n\xi} \left[ (m_2 n^{-1} + m_3 n^{-2}) \phi'(n^{-1}) - \xi^2 N_1(\xi^{-1}) \right] \\ & - \frac{2c n (m_2 + n m_3) b_0 \xi}{\kappa (1-n^2)^2 (n-\xi)} \end{aligned}$$

where

$$N_1(\xi) = -\frac{(X-iY)\xi}{2\pi(1+\kappa)}, \quad b_0 = b + N_1(\xi),$$

$$b = \frac{\kappa E_1 - \nu h \bar{E}_1}{c(k^2 - h^2 \nu^2)},$$

$$E_1 = \nu \overline{N_1(n^{-1})} [n(n^2-2)(m_2 + n m_3) + h].$$

Here, we obtain the solution of the second fundamental problem, when a force  $(X, Y)$  acts on the center of the curvilinear kernel.

### Conclusions

The following results can be discussed :

1. In the theory of two dimensional linear elasticity, one of the most useful techniques for the solution of boundary value problems for a Wkwardly shaped region is to transform the region into one simpler shape.
2. The mapping function (4) maps the curvilinear hole  $C$  in  $xy$ -plane onto the domain outside a unit circle  $\gamma$  in  $\xi$ - plane, where  $z'(\xi) \neq 0$  or  $\infty$  for  $|\xi| > 1$ .
3. The physical interest of the mapping comes from that all the references in this domain is a special case of this map, and many special cases can be derived from this work.
4. One of the best methods of obtaining the solutions in the theory of elasticity analytically is the complex variable method which gives the solution directly and its function is considered a solution of Fredholm integral equation.

$$\phi'(\xi) + \frac{1}{2\pi} \int_{\gamma} K(\xi, \sigma) \phi'(\sigma) d\sigma = A'(\xi) - kw'(\xi)$$

where

$$k = \frac{\overline{\phi'(0)}}{w'(0)}, \quad K(\xi, \sigma) = \frac{w(\sigma) - w(\xi) - (\sigma - \xi) w'(\xi)}{w'(\sigma) (\sigma - \xi)^2}.$$

5. This work is considered as a generalization of the work of the infinite plate with a curvilinear hole  $C$  under certain conditions<sup>4-6</sup>.

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# Motions and affine motions in Finsler, Randers and Kropina spaces

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## Abstract

The paper has been devoted to the study of infinitesimal motions and infinitesimal affine motions in a Finsler space with special reference to Randers and Kropina spaces. The necessary and sufficient conditions under which an infinitesimal motion in the associated Riemannian space, of a Randers space,  $F_n^r$ , or of a Kropina space  $F_n^k$ , is an infinitesimal motion in  $F_n^r$  or in  $F_n^k$  and *vice-versa* have been obtained. Similar results for infinitesimal affine motions have also been derived. The properties of infinitesimal motions in hypersurfaces of Randers and Kropina spaces have been explored.

(Keywords : Finsler geometry/Randers space/Kropina space)

## 1. Introduction

Let  $F_n$  be an  $n$ -dimensional Finsler space characterised by the metric function  $F(x, y)$  which satisfies the conditions (A), (B), (C) given by Rund<sup>1</sup> (pages 3, 5). Suppose  $v^i(x)$  is a vectorfield of class  $c^2$  defined over a region  $R$  of  $F_n$ . With this vector field we associate an infinitesimal transformation given by

$$(1.1) \quad \bar{x}^i = x^i + v^i(x) d\tau,$$

where  $d\tau$  is regarded as an infinitesimal constant. The Lie derivative (in  $F_n$ ), of a mixed tensor  $T^{i_1 \dots i_r} j_1 \dots j_s(x, y)$ , for the infinitesimal transformation (1) has been obtained in (1) (page 174). This is given by

$$(1.2) \quad D_L T^{i_1 \dots i_r} j_1 \dots j_s = v^k T^{i_1 \dots i_r} j_1 \dots j_s | k +$$

$$\frac{\partial T^{i_1 \dots i_r j_1 \dots j_s}}{\partial y^k} v_{lk}^h y^k - \sum_v T^{i_1 \dots i_{v-1} k i_{v+1} \dots i_r j_1 \dots j_s} v_{lk}^h + \sum_{\mu} T^{i_1 \dots i_r j_1 \dots j_{\mu-1} k j_{\mu+1} \dots j_s} v_{lk}^h | j_{\mu}.$$

where the symbol 1 stands for Cartan's covariant derivation (Rund<sup>1</sup>, page 43).

In particular, the Lie derivative of the metric tensor  $g_{ij}(x, y)$ , of  $F_n$ , is given by

$$(1.3) \quad \frac{D}{L} g_{ij}(x, y) = 2 A_{ijh} v_{lk}^h l^k + v_{j|i} + v_{i|j},$$

where  $A_{ijk} = FC_{ijk} = F \frac{1}{2} \frac{\partial g_{ij}(x, y)}{\partial y^k}$  and  $l^k = \frac{y^k}{F}$  is the element of support.

The infinitesimal transformation (1.1) is called an infinitesimal motion in  $F_n$  if

$$(1.4) \quad \frac{D}{L} g_{ij}(x, y) = 0.$$

On the other hand (1.1) is called an infinitesimal affine motion if

$$(1.5) \quad \frac{D}{L} (\Gamma_{jk}^{*i}) = 0,$$

where  $\Gamma_{jk}^{*i}$  are the components of the Cartan's connection coefficients of  $F_n$ .

We now consider a Riemannian space  $V_n$  equipped with the metric tensor  $a_{ij}(x)$  and let  $b_i(x)$  be the covariant vector field defined on the domain of the manifold of  $V_n$ . Suppose, further, that

$$\alpha = (a_{ij}(x) y^i y^j)^{\frac{1}{2}} \text{ and } \beta = b_i(x) y^i, \text{ } y^i \text{ being a vector field.}$$

We consider a Finsler space whose fundamental function is a function,  $L$ , of  $\alpha, \beta$ . The function  $F(x, y) = L(\alpha, \beta)$ , satisfying the usual conditions of Finsler metric is called  $(\alpha, \beta)$ -metric. Two important examples of such a metric are



$$(1.6) \quad L_1(\alpha, \beta) = \alpha + \beta \quad (\text{Randers metric}^2),$$

$$(1.7) \quad L_2(\alpha, \beta) = \frac{\alpha^2}{\beta} \quad (\text{Kropina metric}^3)$$

The manifolds equipped with these metrics are called Randers and Kropina spaces respectively. The Riemannian space,  $V_n$ , is called associated Riemannian space.

In the following sections of this paper we shall find the necessary and sufficient conditions under which an infinitesimal motion of the associated Riemannian space is an infinitesimal motion of the Randers and Kropina spaces and *vice versa*. We shall, further, determine the conditions under which an affine motion of the associated Riemannian space is an affine motion in the Randers or Kropina space and *vice versa*.

## 2. Motion in a Finsler Space

It is clear from the definition of Lie derivative given by (Rund<sup>1</sup>, page 174) that it does not in any way depend on the space in which it has been defined. However, in the existing literature the expressions of Lie derivatives of various quantities have been expressed in terms of metrics and connection parameters of the space in which these quantities have been introduced.  $a_{ij}$ , being the components of an arbitrary second order covariant tensor in the Randers or Kropina spaces, its Lie derivatives in  $V_n$  and  $F_n$  will be denoted by  $D_R a_{ij}$  and  $D_L a_{ij}$  respectively. We shall now prove the following :

$$\text{Theorem (2.1)} \quad D_L a_{ij} = D_R a_{ij}$$

*Proof*: Using the equation (1.2) we find that

$$(2.1) \quad D_L a_{ij} = v^k a_{ij|k} + a_{kj} v_{|i}^k + a_{ik} v_{|j}^k.$$

Since both  $a_{ij}$  and  $v_k$  are independent of  $y$ , the relations

$$a_{ij|k} = \frac{\partial a_{ij}}{\partial x^k} - a_{rj} \Gamma_{ik}^{*r} - a_{ir} \Gamma_{jk}^{*r}, \quad v_{|i}^k = \frac{\partial v^k}{\partial x^i} + v^r \Gamma_{ri}^{*k},$$

the corresponding relation for  $v_{|j}^k$ , the symmetric property of  $\Gamma_{ik}^{*r}$  and the eqn. (2.1) give

$$(2.2) \quad D_L a_{ij} = \frac{\partial a_{ij}}{\partial x^k} v^k + a_{kj} \frac{\partial v^k}{\partial x^i} + a_{ik} \frac{\partial v^k}{\partial x^j} = a_{kj} v^k_{;i} + a_{ik} v^k_{;j} = \hat{v}_{i;j} + \hat{v}_{j;i} = D_L a_{ij}$$

(Yano<sup>4</sup> page 5), where  $\hat{v}_i = a_{ij} v^j$  and the symbol; stands for the covariant derivation with respect to the Christoffel's symbols of the Riemannian space  $V_n$ . This proves the theorem.

A calculation based on eqn. (1.2) and the fact

$$y^i_{|h} = 0 \text{ gives}$$

$$\text{Lemma (2.1)} \quad D_L y^i = 0$$

If  $T^i_j$  is an arbitrary tensor field defined over the manifold of the Finsler space  $F_n$  then a simple calculation based on eqn. (1.2) and the definition  $v^i_{|k}$  will prove the following:

*Lemma (2.2) :*  $\hat{\partial}_k (D_L T^i_j) = D_k (\hat{\partial}_k T^i_j)$ , where  $\hat{\partial}_k$  stands for partial derivative with respect to  $y^k$ .

The well known relations :

$$F^2 = g_{ij} y^i y^j, \quad g_{ij} = \frac{1}{2} \frac{\partial}{\partial y^i} \frac{\partial}{\partial y^j} F^2$$

and the lemmas (2.1) and (2.2) yield

$$(2.3) \quad \text{(a) } 2F D_L F = (D_L g_{ij}) y^i y^j \text{ and (b) } D_L g_{ij} = \frac{\partial}{\partial y^i} \frac{\partial}{\partial y^j} (F D_L F),$$

which prove the followings :

**Theorem (2.2) :** The necessary and sufficient condition that (1.1) is an infinitesimal motion in  $F_n$  is that  $D_L F = 0$ .

(2.3) A direct calculation based on the relations

$$l_i = \dot{\partial}_i F, \quad l_i y^i = F$$

and Lemmas (2.1) and (2.2) give

$$(2.4) \quad (a) \quad \frac{D}{L} l_i = \frac{\dot{\partial}_i}{L} (D F) \text{ and } (b) \quad \frac{(D}{L} l_i) y^i = \frac{D}{L} F,$$

which prove the followings :

*Theorem (2.3)* The necessary and sufficient condition that (1.1) is an infinitesimal motion in  $F_n$  is that  $\frac{D}{L} l_i = 0$ .

A direct calculation based on eqn. (1.2), and identities  $l_{i|h} = 0$ ,  $F \dot{\partial}_j l_i = g_{ij} - l_i l_j$  gives

$$\textit{Theorem (2.4)} \quad \frac{D}{L} l_i = (v_{i|k} + v_{k|i}) l^k - v_{h|k} l^h l^k l_i,$$

where  $v_i = g_{ij}(x, y) v^j$ .

Theorems (2.3) and (2.4) yield the following :

*Theorem (2.5)* : The necessary and sufficient condition that (1.1) is an infinitesimal motion in  $F_n$  is that

$$(2.5) \quad (v_{i|k} + v_{k|i}) l^k = 0.$$

If (1.1) is an infinitesimal motion in  $F_n$  then  $v^i(x)$  is called a Killings vector in  $F_n$ . We shall consider the following special cases of the Killings vector.

*Case (1)* : Let  $v^i(x)$  be concurrent in  $F_n$  (Matsumoto and Egachi<sup>5</sup>). Then

$$(2.6) \quad (a) \quad v_{|j}^i = -\delta_j^i \text{ and } (b) \quad v^i | j = 0,$$

where the symbol  $|$  has its usual meaning given in Matsumoto and Egachi<sup>5</sup>.

The relation (2.6)(a) gives  $v_{i|k} = -g_{ik}$ , which on substitution in (2.5) gives  $l_i = 0$ , which is a contradiction.

Hence we have the following :

*Theorem (2.6) :* If (1.1) is an infinitesimal motion in  $F_n$  then the Killings vector  $v^i(x)$  can not be concurrent in  $F_n$  .

*Case (ii) :* Let  $v^i(x)$  be concircular in  $F_n$  . Then from Prasad *et al.*<sup>6</sup>

$$(2.7) \quad (a) \quad v_{ij}^i = k_j v^i + \rho \delta_j^i \quad (b) \quad v^j | j = 0 ,$$

where  $k_j(x)$ ,  $\rho(x)$  are components of non-null covariant vector and non-zero scalar invariant functions. The relation (2.7) a, when substituted in (2.5) gives

$$(2.8) \quad 2\rho l_i + k_0 v_i + v_0 k_i = 0 ,$$

where  $k_0 = k_i l^i$  and  $v_0 = v_j l^j$  .

Transvection of (2.8) by  $l^i$  gives  $\rho = -k_0 v_0$  . Therefore,  $\rho \neq 0$  implies  $k_0 \neq 0$ ,  $v_0 \neq 0$ . The equation (2.8) proves the following.

*Theorem (2.7) :* If (1.1) is an infinitesimal motion in  $F_n$  and the Killings vector  $v^i(x)$  is concircular in  $F_n$  then  $k_i$  is a linear combination of  $l_i$  and  $v_i$  .

*Case (iii) Let  $v^i(x)$  be semi-parallel in  $F_n$  . Then from Singh and Prasad<sup>7</sup>*

$$(2.9) \quad (a) \quad v_{ij} = (\lambda g_{ij} + \epsilon v_i v_j) \quad \text{and} \quad (b) \quad C_{jk}^i v^j = 0 ,$$

where  $\lambda(x)$ ,  $\epsilon(x)$  are non-zero scalar functions and

$$(2.10) \quad C_{jk}^i = g^{hi} C_{jhk} = g^{hi} \frac{1}{2} \frac{\partial g_{jh}}{\partial y^k} .$$

The relation (2.7) a and (2.5) give

$$(2.11) \quad v_i(x) = - \frac{\lambda}{\epsilon v_0} l_i .$$

Differentiating (2.11) with respect to  $y^h$  and using the relation

$$\dot{\partial}_h l_i = \frac{1}{F} (g_{ih} - l_i l_h), \text{ we get}$$

$$\dot{\partial}_h \left( \frac{\lambda}{\in v_0} \right) l_i + \frac{\lambda}{F \in v_0} (g_{ih} - l_i l_h) = 0.$$

Multiplying this relation by  $F$ , transvecting by  $g^{ih}$  and using the relation  $y^h = F l^h$  and the fact that  $\frac{\lambda}{\in v_0}$  is positively homogeneous of degree zero in  $y^i$  we find  $\frac{\lambda}{\in v_0} (n-1) = 0$ , which gives  $\lambda = 0$  for  $n \neq 1$ . This a contradiction. Hence we have the following :

*Theorem (2.8) :* If (1.1) is an infinitesimal motion in (1.1) then the Killings vector  $v^i(x)$  can not be semi-parallel in  $F_n$  for  $n \neq 1$ .

### 3. Motions in Randers and Kropina Spaces

The eqn. (1.6) gives the metric function,  $F(x, y)$ , of the Randers space in the form :

$$(3.1) \quad F(x, y) = \alpha + \beta,$$

The partial differentiation of (3.1) with respect to  $y^i$  and the application of the relations :

$$(3.2) \quad l_i = \dot{\partial}_i F, \quad p_i = \dot{\partial}_i \alpha, \quad b_i = \dot{\partial}_i \beta$$

$$\text{give} \quad l_i = p_i + b_i,$$

which yields

$$(3.3) \quad \frac{D}{L} l_i = \frac{D}{L} p_i + \frac{D}{L} b_i.$$

By Theorem (2.1) the infinitesimal transformation (1.1) is an infinitesimal motion in  $V_n$  if and only if (Yano<sup>4</sup>, page 5)

$$(3.4) \quad \frac{D}{L} a_{ij} = \frac{D}{R} a_{ij} = 0.$$

Proceeding, in  $V_n$ , in a manner similar to the proof of Theorems (2.2) and (2.3) we get the following :

*Theorem (3.1)* : The transformation (1.1) is an infinitesimal motion in the associated Riemannian space  $V_n$  iff  $D \alpha = 0$  and  $L$

*Theorem (3.2)* : The transformation (1.1) is an infinitesimal motion in the associated Riemannian space  $V_n$  iff  $D p_i = 0$ .  $L$

The equation (3.3) and Theorem (3.2) yield :

*Theorem (3.3)* : The necessary and sufficient condition that an infinitesimal motion in the associated Riemannian space  $V_n$  be an infinitesimal motion in the Randers space  $F_n$  or vice-versa is that  $D b_i = 0$ .  $L$

We now assume that  $F_n$  is a Kropina space. By relation (1.7) its metric function is given by

$$(3.5) \quad F(x, y) = \frac{\alpha^2}{\beta}.$$

The Lie derivative of this relation gives

$$(3.6) \quad \frac{D F}{L} = 2\rho \left( \frac{D \alpha}{L} \right) - \rho^2 \left( \frac{D \beta}{L} \right), \text{ and } \rho = \frac{\alpha}{\beta}.$$

Theorems (2.2), (3.1), the relation (3.6) and the fact  $\rho \neq 0$  give the following :

*Theorem (3.4)* : The necessary and sufficient condition that an infinitesimal motion in the associated Riemannian space  $V_n$  be an infinitesimal motion in the Kropina space  $F_n$  or vice versa is that  $D \beta = 0$ .  $L$

The relations  $\beta = b_i y^i$ ,  $b_i = \dot{\partial}_i \beta$  and Lemmas (2.1), (2.2) give

$$(3.7) \quad (a) \frac{D \beta}{L} = \left( \frac{D b_i}{L} \right) y^i \quad (b) \frac{D b_i}{L} = \dot{\partial}_i \left( \frac{D \beta}{L} \right).$$

The Theorem (3.4), therefore, reduces to

*Theorem (3.5)* : The necessary and sufficient condition that an infinitesimal motion in the associated Riemannian space  $V_n$  be an infinitesimal motion in the Kropina space  $F_n$  or vice versa is that  $D \frac{b_i}{L} = 0$ .

Theorem (3.3) and (3.5) yield the following :

*Theorem (3.6)* : Let the Randers and Kropina metrics defined, on an n-dimension manifold, have the same associated Riemannian metric  $\alpha$  and same linear form  $\beta = b_i(x) y^i$ . If  $D \frac{b_i}{L} = 0$  then the following three statements are equivalent :

- (a) The relation (1.1) is an infinitesimal motion in the associated Riemannian space.
- (b) The relation (1.1) is an infinitesimal motion in the Randers space.
- (c) The relation (1.1) is an infinitesimal motion in the Kropina space.

#### 4. Motions in Hypersurfaces of Randers and Kropina Spaces

Consider a hypersurface  $F_{n-1} : x^i = x^i(u^\alpha)$ ; ( $i = 1, \dots, n$ ;  $\alpha = 1, \dots, n-1$ ) of a Finsler space  $V_n$ . The components  $g_{\alpha\beta}$ ,  $g_{ij}$  of the metric tensors of  $F_{n-1}$ ,  $F_n$  are related by

$$(4.1) \quad g_{\alpha\beta}(u, v) = g_{ij}(x, y) B_\alpha^i B_\beta^j,$$

where  $B_\alpha^i = \frac{\partial x^i}{\partial u^\alpha}$  and  $y^i = B_\alpha^i v^\alpha$ .

It has been shown in literature<sup>8,9</sup> that  $F_{n-1}$  is a Randers space whenever  $F_n$  is Randers space and  $F_{n-1}$  is a Kropina space whenever  $F_n$  is Kropina space. The metric tensors of the associated Riemannian spaces  $V_{n-1}$ ,  $V_n$ , of  $F_{n-1}$  and  $F_n$  respectively, whether they are Randers or Kropina, are related by

$$(4.2) \quad a_{\alpha\beta} = a_{ij} B_\alpha^i B_\beta^j.$$

It has been shown in Rund<sup>1</sup>, (page 176) that

$$(4.3) \quad D \frac{a}{L} B_\alpha^i = 0,$$

where  $\overset{a}{D}_L$  stands for Lie derivative in  $F_{n-1}$ , for the infinitesimal transformation (1.1). It may

be noted that  $\overset{a}{D}_L = \overset{a}{D}_L$ , for the quantities of  $F_n$  (Rund<sup>1</sup>, page 176).

This fact and the relations (4.1), (4.2) and (4.3) yield.

$$(4.4) \quad (a) \overset{a}{D}_L g_{\alpha\beta} = (\overset{a}{D}_L g_{ij}) B_{\alpha}^i B_{\beta}^j \quad \text{and} \quad (b) \overset{a}{D}_L a_{\alpha\beta} = (\overset{a}{D}_L a_{ij}) B_{\alpha}^i B_{\beta}^j$$

The relations (4.4)a, (4.4)b and Lemma (2.1) show that (1.1) is an infinitesimal motion in  $F_{n-1}$ , whenever it is an infinitesimal motion in  $F_n$  and it is an infinitesimal motion in  $V_{n-1}$  whenever it is an infinitesimal motion in  $V_n$ . Using these facts and Theorem (3.6) we get the following :

**Theorem (4.1) :** Let a Randers space  $\overset{r}{F}_n$  and a Kropina space  $\overset{k}{F}_n$  defined on a manifold have the same associated Riemannian space  $V_n$  and the same linear form  $\beta$ . Suppose further that the same set of equations  $x^i = x^i(u^\alpha)$  ( $i = 1, \dots, n$ ;  $\alpha = 1, \dots, n-1$ ) represent the hypersurfaces  $\overset{r}{F}_{n-1}$ ,  $\overset{k}{F}_{n-1}$ ,  $\overset{r}{V}_{n-1}$  of  $\overset{r}{F}_n$ ,  $\overset{k}{F}_n$ ,  $\overset{k}{V}_n$  respectively. If  $\overset{a}{D}_L b_i = 0$  and any one of

the three conditions (a), (b), (c) of Theorem (3.6) is satisfied then the remaining two conditions and the condition (d), (e), (f) mentioned below are also satisfied.

(d) The relation (1.1) is an infinitesimal motion in  $\overset{r}{V}_{n-1}$

(e) The relation (1.1) is an infinitesimal motion in  $\overset{r}{F}_{n-1}$

(f) The relation (1.1) is an infinitesimal motion in  $\overset{k}{F}_{n-1}$ .

## 5. Affine Motion in a Finsler Space

If  $X_j^i$  is an arbitrary mixed tensor defined on the manifold of  $F_n$  then we have the following commutation formula (Yano<sup>4</sup>, page 189).



$$(5.1) \quad (D_L X_j^i)_k - D_L (X_{jk}^i) = -X_j^r (D_L \Gamma_{rk}^{*i}) + X_r^i (D_L \Gamma_{jk}^{*r}) + \frac{\partial X_j^i}{\partial y^r} (D_L \Gamma_{pk}^{*r}) y^p.$$

Using this relation for the metric tensor  $g_{ij}$  and assuming that infinitesimal transformation (1.1) is an infinitesimal motion we get

$$(5.2) \quad g_{rj} (D_L \Gamma_{ik}^{*r}) + g_{ir} (D_L \Gamma_{jk}^{*r}) + 2C_{ijr} (D_L \Gamma_{pk}^{*r}) y^p = 0,$$

where we have used the facts  $g_{jk} = 0$ ,  $D_L g_{ij} = 0$  and  $C_{ijr}$  is defined by (2.10).

Carrying out two successive cyclic interchanges of the indices  $i, j, k$  in (5.2) adding the first relation thus obtained to (5.2) and subtracting the last relation from this sum we get

$$(5.3) \quad g_{ij} (D_L \Gamma_{ki}^{*r}) + C_{ijr} (D_L \Gamma_{pk}^{*r}) y^p + C_{jkr} (D_L \Gamma_{pi}^{*r}) y^p \\ - C_{kir} (D_L \Gamma_{pj}^{*r}) y^p = 0,$$

where we have used the fact that  $\Gamma_{ij}^{*r}$ ,  $g_{ij}$  are symmetric in  $i, j$ , Transvecting this relation by  $y^i$  and using the identity

$$C_{ijr} y^i = C_{jir} y^i = C_{jri} y^i = 0, \text{ we get}$$

$$(5.4) \quad g_{rj} (D_L \Gamma_{ki}^{*r}) y^i + C_{jkr} (D_L \Gamma_{pi}^{*r}) y^p y^i = 0.$$

Transvection of (5.4) by  $y^k$  gives

$$(5.5) \quad (D_L \Gamma_{ki}^{*r}) y^k y^i = 0.$$

Again a simple calculation based on equations (5.5), (5.4), (5.3) (in this order) will give

$$(5.6) \quad D_L (\Gamma_{ki}^{*r}) = 0.$$

Using (1.5) we get the following :

*Theorem (5.1) :* An infinitesimal motion in a Finsler space is an infinitesimal affine motion.

Lemma (2.2), the relation  $C_{ijk} = \frac{1}{2} (\dot{\partial}_k g_{ij})$

and equation (1.4) yield

*Theorem (5.2) :* If (1.1) is an infinitesimal motion in  $F_n$  then  $D_L (C_{ijk}) = 0$ .

Defining  $C_{ijk|_o} = C_{ijk|h} y^h$ , using relation (5.1) for  $C_{ijk}$  and applying Lemma (2.1) and Theorems (5.1), (5.2), we get :

*Theorem (5.3) :* If (1.1) is an infinitesimal motion then  $D_L C_{ijk|_o} = 0$ . The connection coefficients  $G_{jk}^i$  of Berwald and  $\Gamma_{jk}^{*i}$  of Cartan are related by (Rund<sup>1</sup>, page 79).

$$G_{jk}^i = \Gamma_{jk}^{*i} + C_{jk|_o}^i.$$

*Theorems (5.1) and (5.3) yield*

*Theorem (5.4) :* If (1.1) is an infinitesimal motion in  $F_n$  then

$$D_L G_{jk}^i = 0.$$

## 6. Affine Motions in Randers and Kropina Spaces

It has been proved by (Yano<sup>4</sup>, page 51) that an infinitesimal motion in a Riemannian space  $V_n$  is an affine motion in  $V_n$ .

We assume that a Randers space  $F_n^r$  and a Kropina space  $F_n^k$  have the same associated Riemannian space  $V_n$  and same linear form  $\beta = b_i y^i$ .

Theorem (3.3), (3.5) and (5.1) and the property quoted in the beginning of this section give the following :

*Theorem (6.1)* : If for the infinitesimal transformation (1.1)  $D \frac{b_i}{L} = 0$  and any one of the three conditions (a), (b), (c) mentioned in Theorem (3.6) is satisfied then the remaining two conditions and the conditions (g), (h), (i) mentioned below are also satisfied.

(g) The relation (1.1) is an affine motion in  $V_n$  .

(h) The relation (1.1) is an affine motion in  $F_n^r$  .

(i) The relation (1.1) is an affine motion in  $F_n^k$  .

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## **Free convection in MHD flow of a rotating viscous liquid in porous medium past a vertical porous plate**

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### **Abstract**

In the present paper, free convection effect in the unsteady flow of an incompressible, electrically, conducting viscous, rotating liquid in a porous medium past an isothermal vertical porous plate with constant suction normal to the plate under the influence of uniform magnetic field applied perpendicular to the flow has been studied. The effect of porosity parameter, rotation parameter, magnetic parameter, Grashof number, frequency parameter on transient primary velocity, secondary velocity, temperature distribution and rate of heat transfer has been discussed.

(Keywords : porous medium/magnetic field/rotating viscous liquid).

### **Introduction**

Free convection problem has attracted considerable amount of interest because of its importance in atmospheric and oceanic circulations, nuclear reactors, powder transformers etc. Extensive review of the free convection flows is available in literature<sup>1-3</sup>. Several authors<sup>4-7</sup> have discussed flow in rotating system in presence in magnetic field. Jana and Dutta<sup>8</sup> and Palec and Daguenet<sup>9</sup> have studied problems on convective flow of rotating fluids in absence of magnetic field. Studies on MHD flow of viscous fluids in rotating system have also been reported by several authors<sup>10-13</sup>. Recently, Seth and Banerjee<sup>14</sup> have studied combined free and forced convective flow of a viscous fluid in rotating channel in the presence of a uniform transverse magnetic field applied parallel to the axis of rotation. More recently, Phukan<sup>15</sup> has discussed two dimensional MHD free convective oscillatory flow of a viscous fluid past a semi-infinite vertical flat plate. In the present paper, we propose to discuss the combined effect of constant suction and heat source on free convective MHD flow of a rotating viscous liquid in porous medium past an infinite vertical isothermal porous plate.

### Formulation of the Problem

Let  $x$ -axis and  $y$ -axis be in the plane of the plate and  $z$ -axis normal to the plate with velocity components  $u, v, w$  of the fluid in these directions respectively. Both the liquid and the plate are considered in a state of rigid body rotation about  $z$ -axis with uniform angular velocity  $\Omega$ . Further we assume that the uniform magnetic field  $B_0 = \mu_e \vec{H}$ , where  $\vec{H} = (0, 0, H_0)$  is applied in the  $z$ -direction. The constant heat source  $Q$  is assumed at  $z = 0$  and the suction velocity at the plate is  $w = -w_0$  where  $w_0$  is a positive real number. In this analysis buoyancy effect, Hall effect, effect due to perturbation of the field, induced magnetic field and polarization effect are ignored.

Since the plate is infinite in extent, all physical variables depend on  $z$  and  $t$  only. Besides, we take the heat source of absorption type  $Q = -Q_0 (T - T_\infty)$ . In the present configuration, using  $u + iv = q$ , the equations governing the flow (ignoring the stars over them introduced ahead) are

$$\frac{\partial q}{\partial t} - \frac{\partial q}{\partial z} + \left( M^2 + \frac{1}{k_0} + 2iE \right) (q - U) = \frac{\partial U}{\partial t} + \frac{\partial^2 q}{\partial z^2} + G_r T \quad (1)$$

$$\frac{\partial^2 T}{\partial z^2} + P_r \frac{\partial T}{\partial z} - P_r \frac{\partial T}{\partial t} - \alpha_0 T = 0 \quad (2)$$

The non-dimensional boundary conditions are

$$\left. \begin{aligned} q &= (1 + \epsilon e^{int}), \quad T = (1 + \epsilon e^{int}, n > 0) & \text{at } z = 0 \\ q &= (1 + \epsilon e^{int}, n > 0), \quad T \rightarrow 0 & \text{at } z \rightarrow \infty \end{aligned} \right\} \quad (3)$$

The non-dimensional quantities introduced in the above equations are defined as :

$$z^* = \frac{w_0 z}{v}, \quad t^* = \frac{w_0^2 t}{v}, \quad u^* = \frac{u}{U_0}, \quad n^* = \frac{vn}{w_0^2}, \quad q^* = \left( \frac{u}{U_0} + i \frac{v}{U_0} \right),$$

$$T = \frac{(T - T_\infty)}{(T_w - T_\infty)}, \quad P_r = \frac{\nu \rho c_p}{K}, \quad E = \frac{\Omega \nu}{w_0^2}, \quad G_r = \frac{\nu g \beta_0 (T_w - T_\infty)}{U_0 w_0^2}$$

$$M^2 = \frac{\sigma \mu_e^2 H_0^2 \nu}{\rho w_0^2}$$

where  $P_r$  : Prandtl number,  $G_r$  : Grashof number,  $M$  : magnetic parameter,  $E$  : rotation parameter,  $k$  : permeability parameter,  $\alpha_0$  : heat source parameter,  $U$  : free stream velocity and other physical quantities have their usual meanings.

### Solution of the Problem

In order to solve the eqn. (1) and (2), we assume the velocity and temperature of the liquid in the neighbourhood of the plate as

$$q = (1 - q_0) + \epsilon (1 - q_1) e^{int} \quad (4)$$

$$T = T_0 + \epsilon T_1 e^{int} \quad (5)$$

where  $(1 - q_1) e^{int} = (M_r + iM_i) (\cos nt + i \sin nt)$

and  $T_1 e^{int} = (T_r + iT_i) (\cos nt + i \sin nt)$

Also for the free stream (when  $\epsilon \ll 1$ )

$$U(t) = (1 + \epsilon e^{int}) \quad (6)$$

The transient velocity and temperature profiles can be deduced from the eqn. (4) and (5)

for  $nt = \frac{\pi}{2}$ . Hence we have

$$u(z, t) = u_0(z) - \epsilon M_i \quad (7)$$

$$T = T_0 - \epsilon T_1 \quad (8)$$

where  $u_0(z) + iv_0(z) = (1 - q_0)$

Using eqn. (4), (5) and (6) in eqn. (1) and (2) and equating harmonic and non-harmonic terms, we get four equations. On solving these equations under corresponding boundary conditions, we obtain  $q_0$ ,  $q_1$ ,  $T_0$  and  $T_1$ .

Substituting the values of  $q_0$  and  $q_1$  in the eqn. (4) and the values of  $T_0$  and  $T_1$  in the eqn. (5), we obtain

$$q = 1 - D_1 \left( e^{-h_2 z} - e^{-H_6 z} \right) + \epsilon \left[ 1 - D_2 \left( e^{-H_4 z} - e^{-H_8 z} \right) \right] e^{int} \quad (9)$$

and 
$$T = e^{-h_2 z} + \epsilon e^{(H_4 z - int)} \quad (10)$$

From (9), the primary velocity  $u$  and secondary velocity  $v$  are obtained as

$$u = 1 - \frac{G_r A \alpha_1}{\alpha_1^2 + (2E)^2} - \frac{2EG_r}{\alpha_1^2 + (2E)^2} e^{-A_2 z} \sin B_2 z + \epsilon (B \cos nt - C \sin nt) \quad (11)$$

$$v = \frac{2EAG_r}{\alpha_1^2 + (2E)^2} - \frac{G_r \alpha_1}{\alpha_1^2 + (2E)^2} e^{-A_2 z} \sin B_2 z + \epsilon (B \sin nt + C \cos nt) \quad (12)$$

where  $2h_2 = P_r + \sqrt{D_0}$ ,  $D_1 = \frac{G_r(\alpha_1 - i2E)}{\alpha_1^2 + 2E^2}$ ,  $D_2 = \frac{G_r[\alpha_2 - i(2E + n)]}{\alpha_2^2 + (2E + n)^2}$

$$M_1 = M^2 + \frac{1}{k_0}, \quad D_0 = P_r^2 + 4\alpha_0, \quad H_4 = A_1 + iB_1 = \frac{1}{2} \left[ P_r + \sqrt{D_0 + i4nP_r} \right],$$

$$H_6 = A_2 + iB_2 = \frac{1}{2} \left[ 1 + \sqrt{1 - 4(M_1 + i2E)} \right]$$

$$H_8 = A_3 + iB_3 = \frac{1}{2} \left[ 1 + \sqrt{1 - 4(M_1 + i(2E + n))} \right], \quad \alpha_1 = h_2^2 - h_2 + M_1$$

$$A_1 = \frac{P_r}{2} + \frac{1}{2\sqrt{2}} \left[ D_0 + \sqrt{D_0^2 + (4nP_r)^2} \right]^{1/2}, \quad B_1 = \frac{1}{2\sqrt{2}} \left[ \sqrt{D_0^2 + (4nP_r)^2} - D_0 \right]^{1/2}$$

$$A_2 = \frac{1}{2} + \frac{1}{2\sqrt{2}} \left[ D_3 + \sqrt{D_3^2 + (8E)^2} \right]^{1/2}, \quad B_2 = \frac{1}{2\sqrt{2}} \left[ \sqrt{D_3^2 + (8E)^2} - D_3 \right]^{1/2}$$

$$A_3 = \frac{1}{2} + \frac{1}{2\sqrt{2}} \left[ D_3 + \sqrt{D_3^2 + (8E + 4n)^2} \right]^{1/2}$$

$$B_3 = \frac{1}{2\sqrt{2}} \left[ \sqrt{D_3^2 + (8E + 4n)^2} - D_3 \right]^{1/2}, \quad A = e^{-h_2 z} - C e^{-h_2 z} \cos B_2 z,$$

$$D_3 = 1 + 4M_1, \quad B = 1 \frac{G_r \alpha_2 K_1}{\alpha_2^2 + (2E + n)^2} + \frac{(2E + n) K_2}{\alpha_2^2 + (2E + n)^2}$$

$$C = \frac{(2E + n) K_1}{\alpha_2^2 + (2E + n)^2} + \frac{G_r \alpha_2 K_2}{\alpha_2^2 + (2E + n)^2}, \quad K_1 = e^{-A_2 z} \cos B_2 z - e^{-A_3 z} \cos B_3 z$$

$$\text{and} \quad K_2 = e^{-A_3 z} \sin B_3 z + e^{-A_2 z} \sin B_2 z$$

### Heat Transfer and Skin Friction

The rate of heat transfer at the plate in terms of Nusselt number  $Nu$  is

$$Nu = - \left( \frac{\partial T}{\partial z} \right)_{z=0} = h_2 + \epsilon H_4 e^{int} \quad (13)$$

The skin friction  $S_k$  at the plate is

$$\begin{aligned} S_k &= \left( \frac{\partial q}{\partial z} \right)_{z=0} = \left( \frac{\partial q_0}{\partial z} \right)_{z=0} + \epsilon e^{int} \left( \frac{\partial q_1}{\partial z} \right)_{z=0} \\ &= (H_6 - h_2) D_1 + \epsilon D_2 (H_8 - H_4) e^{int} \end{aligned} \quad (14)$$

### Discussion

The numerical calculations for transient velocity  $u$ , the transient secondary velocity  $v$ , transient primary temperature  $T_p$ , transient secondary temperature  $T_s$  and transient rate of heat transfer  $Nu$  have been obtained to observe the physical significance and the mystery of the problem. To be realistic, Prandtl number is chosen as 0.71 (for water vapour) and 7.0 (for water) approximately at 1 atmosphere and 25°C. From physical point of view,  $G_r > 0$  corresponds to cooling of the plate and  $G_r < 0$  corresponds to heating of the plate by free convection currents.



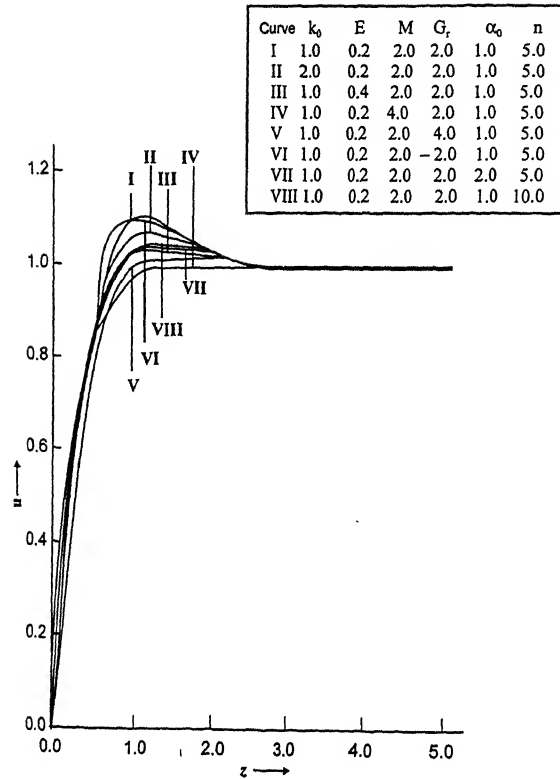


Fig. 1 – Transient primary velocity.  
( $P_r = 0.71$ ,  $\epsilon = 0.02$ , and  $nt = \pi/2$ )

The non-dimensional transient primary velocity profiles  $u$  vs.  $z$  are shown in Fig. 1 to observe the effect of permeability parameter  $k_0$ , rotation parameter  $E$ , magnetic parameter  $M$ , heat source parameter (absorption type)  $\alpha_0$ , frequency parameter  $n$  and Grashof number  $G_r$  at  $P_r = 0.71$ ,  $\epsilon = 0.01$  and  $nt = \frac{\pi}{2}$ . It is observed that the transient primary velocity  $u$  increases regressively and after attaining the maximum value decreases asymptotically and ultimately attains steady state. It is observed that it decreases with the increase in  $z$  when there is an increase in  $k_0$  or  $E$  or  $M$  or  $\alpha_0$  or  $n$ . In addition it is noted that the transient primary velocity  $u$  increases with the cooling of the plate  $G_r > 0$  by free convection currents. The reverse effects are observed with the heating of the plate  $G_r < 0$ .

Similar effects of these parameters ( $k_0$ ,  $E$ ,  $M$ ,  $\alpha_0$ ,  $n$  and  $G_r$ ) are observed on the transient secondary velocity  $v$ . Therefore, any further discussion about their effect on secondary velocity through a figure or table seems to be redundant.

Table 1 - Transient primary ( $T_P$ ) and secondary ( $T_S$ ) temperature field ( $\epsilon=0.01$  and  $n\tau = \pi/2$ ).

$\alpha_0$	$P_r$	$n$	$10^{-4} \times T_P$				$10^{-2} \times T_S$			
			$y=0$	$y=0.1$	$y=0.2$	$y=0.3$	$y=0$	$y=0.1$	$y=0.2$	$y=0.3$
1.0	0.71	5.0	0.00	0.1641	0.2713	0.3361	1.00	0.8249	0.6819	0.5629
2.0	0.71	5.0	0.00	0.1414	0.2286	0.2773	1.00	0.8079	0.6529	0.5279
-1.0	0.71	5.0	0.00	0.2251	0.3861	0.4972	1.00	0.8569	0.7349	0.6309
-2.0	0.71	5.0	0.00	0.2605	0.4534	0.5912	1.00	0.8699	0.7569	0.6579
1.0	7.00	5.0	0.00	0.2579	0.2191	0.1402	1.00	0.4249	0.1809	0.0769
2.0	7.00	5.0	0.00	0.2533	0.2143	0.1343	1.00	0.4229	0.1789	0.0749
-1.0	7.00	5.0	0.00	0.2687	0.2319	0.1514	1.00	0.4309	0.1859	0.0809
-2.0	7.00	5.0	0.00	0.2743	0.2376	0.1554	1.00	0.4339	0.1879	0.0819
1.0	0.71	10.0	0.00	0.2391	0.2898	0.4441	1.00	0.8769	0.6189	0.4869
2.0	0.71	10.0	0.00	0.2199	0.3411	0.3966	1.00	0.7749	0.6009	0.4659
-1.0	0.71	10.0	0.00	0.2825	0.4567	0.5539	1.00	0.8079	0.6529	0.5279
-2.0	0.71	10.0	0.00	0.3061	0.5014	0.6149	1.00	0.8169	0.6689	0.5469

Table 2 – Transient primary ( $Nu_p$ ) and secondary ( $Nu_s$ ) heat transfer ( $\epsilon=0.01$  and  $nt = \pi/2$ )

$\alpha_0$	$P_r$	$n$	$Nu_p$	$Nu_s$
1.0	0.71	5.0	-0.01139	0.0191
2.0	0.71	5.0	-0.01003	0.0212
-1.0	0.71	5.0	-0.01505	0.0153
-2.0	0.71	5.0	-0.01716	0.0139
1.0	7.00	5.0	-0.03477	0.0853
2.0	7.00	5.0	-0.03431	0.0860
-1.0	7.00	5.0	-0.03572	0.0840
-2.0	7.00	5.0	-0.03621	0.0833
1.0	0.71	10.0	-0.01741	0.0239
2.0	0.71	10.0	-0.01624	0.0254
1.0	0.71	10.0	-0.02004	0.0212
2.0	0.71	10.0	-0.02147	0.0200

Table 1 shows effects of  $\alpha_0$ ,  $P_r$  and  $n$  on non-dimensional transient primary temperature field  $T_p$ , transient secondary temperature field  $T_s$  for different values of  $y$  and Table 2 represents transient primary rate of heat transfer  $Nu_p$  and transient secondary rate of heat transfer  $Nu_s$  at the plate at  $\epsilon=0.01$  and  $nt = \pi/2$ . A deep study of these tables reveal that an increase in absorption type heat source parameter  $\alpha_0$  decreases  $T_p$  and  $T_s$  while increases  $Nu_p$  and  $Nu_s$  but reverse effect is noted for generation type source parameter. It is also observed that an increase in Prandtl number leads to a decrease in  $T_p$  and  $Nu_p$  but an increase in  $T_s$  and  $Nu_s$ . Besides it is noted that an increase in frequency parameter  $n$  leads to an oscillatory effect on  $T_p$ ,  $T_s$ ,  $Nu_p$  and  $Nu_s$  and an increase in  $y$  increases  $T_p$  but decreases  $T_s$ .

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## On the ultradistribution of Mellin transform

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### Abstract

In this paper we deal with the relation between the Mellin and the Fourier transform and its inverse. By introducing these relations, some theorems of ultradistribution for Mellin transform are proved; properties for the testing function space  $\mathcal{Z}$  and its dual  $\mathcal{Z}'$  are also obtained.

(Keywords : Mellin transform/testing function space/ultradistribution)

### Introduction

The relation between the Mellin and the Fourier transform is given by (Erdélyi<sup>1</sup>; p. 305).

$$\mathcal{M}\{f(x); s\} = \mathcal{F}\{f(e^x); is\} \quad (1)$$

One of the form of the Mellin transform is

$$\tilde{f}(is) \triangleq \mathcal{F}\{f(e^x)\} \triangleq \int_{-\infty}^{\infty} f(e^x) e^{sx} dx. \quad (2)$$

Its inverse Mellin transform is defined as

$$f(e^x) \triangleq \mathcal{F}^{-1}\{\tilde{f}(is)\} \triangleq \frac{1}{2\pi} \int_{-\infty}^{\infty} \tilde{f}(is) e^{-sx} ds, \quad (3)$$

where  $\mathcal{F}$  denotes the Fourier transform and  $\mathcal{F}^{-1}$  denotes the inverse Fourier transform.

The object of this paper is to prove the theorems of ultradistributions for Mellin transform. Having introduced the relation between the Fourier and the Mellin transform and its inverse, we prove theorems for a new class  $\mathcal{Z}$  of testing functions and the dual space  $\mathcal{Z}'$  of continuous linear functionals on  $\mathcal{Z}$ . The distributions in  $\mathcal{D}'$  of the Fourier transform are the elements of  $\mathcal{Z}'$ , will be called ultradistribution. Some properties viz. addition,

multiplication by a constant  $\alpha$ , differentiation and transposition of an ultradistribution are derived.

### The Space $\mathcal{Z}$ and its Dual $\mathcal{Z}'$

Let  $\mathcal{Z}$  be the space of entire function  $\psi(z)$  of  $n$ -complex variables such that there exist constants  $C_{m,p}$  and  $a_1, a_2, \dots, a_n$ , such that

$$|z|^p |D^m \psi(z)| \leq C_{m,p} \exp(a_1 |y_1| + \dots + a_n |y_n|), \quad (4)$$

for all  $p = (p_1, p_2, \dots, p_n)$ ,  $p_j \geq 0$  and  $m = (m_1, m_2, \dots, m_n)$ ,  $m_j \geq 0$ . A sequence  $\{\psi_v\}$  is said to converge in the sense of  $\mathcal{Z}$ , iff  $\{\psi_v\}$  converges to a limit function uniformly in every order and there exist constants  $C_{m,p}$  and  $a_1, a_2, \dots, a_n$  independent of  $v$ , s. t.

$$|z|^p |D^m \psi(z)| \leq C_{m,p} \exp(a_1 |y_1| + \dots + a_n |y_n|)$$

for all  $z, y = \text{Im}(z)$ , where  $p, m$  are non-negative integers.

A sequence  $\{\psi_v\}$  of function in  $\mathcal{Z}$  is said to converge in the sense of  $\mathcal{Z}$  iff the following properties are satisfied :

- (i) The sequence  $\{\psi_v\}$  converges to a limit function uniformly on every compact set in the  $z$ -plane.
- (ii) For every  $m \geq 0$ ,  $\{D^m \psi\}$  converges to  $\{D^m \psi_0\}$  uniformly on every compact set in the  $z$ -plane.
- (iii) There exist constants  $C_{m,p}$  and  $a$ , independent of  $v$ , such that

$$|z|^p |D^m \psi_v(z)| \leq C_{m,p} e^{a|y|} \quad (5)$$

for all  $z$  and  $v$ .

The dual of the space  $Z$  is defined as  $Z'$ . Thus,  $Z'$  is the space of all ultradistributions (continuous linear functionals on the space  $Z$ ). The function  $f$  is in  $Z'$  iff it satisfies the following two conditions :

(i) *Linearity* : If  $\phi_1$  and  $\phi_2$  are testing functions in  $Z$  and  $\alpha$  and  $\beta$  are two complex numbers, then

$$(f, \alpha\phi_1 + \beta\phi_2) = \alpha(f, \phi_1) + \beta(f, \phi_2). \quad (5)$$

(ii) *Continuity* : If  $\{\phi_v\}_{v=1}^{\infty}$  converges in  $Z$  to zero, then the sequence of numbers  $\{(f, \phi_v)\}_{v=1}^{\infty}$  converges to zero.

It follows from these two conditions that, if  $\{\phi_v\}_{v=1}^{\infty}$  converges in  $Z$  to a limit function  $\phi$  that is not identically zero then  $\{\phi_v\}_{v=1}^{\infty}$  converges to  $(f, \phi)$ . The Mellin transforms of distribution in  $\mathcal{D}'$  are generalized function in  $Z'$ .

### The Space $Z$ of Testing Functions whose Mellin Transforms are in $\mathcal{D}$

Now we will discuss the properties and theorems which are satisfied by the testing functions space  $Z$ , whose Mellin transforms are in  $\mathcal{D}$ . One of the conditions, which is satisfied by the space  $Z$  is given by (5).

The Mellin transformation cannot be used for arbitrary distributions in  $\mathcal{D}'$ . To be specific, if  $f$  is in  $\mathcal{D}'$  but not in  $S'$ , then, as  $\phi$  transverse  $\mathcal{D}$ , the relation

$$(\tilde{f}, \bar{\phi}) \triangleq 2\pi (f, \bar{\phi}) \quad (6)$$

will certainly have a sense. This is so because  $\phi$  will not be in  $\mathcal{D}$  but will instead traverse some new testing function space. The Mellin transform  $\tilde{f}$  of an arbitrary distribution in  $\mathcal{D}'$  is not, in general, a distribution but is instead another kind of continuous linear functional, which is defined over this new space of testing functions. Such a functional is, at times, called an ultradistribution.

Let  $\phi(s)$  be an arbitrary testing function in  $\mathcal{D}$  whose support is contained in the finite interval  $-a \leq s \leq a$ . Its inverse Mellin transform, in the following manner can be written as an integral over this finite interval.

$$\phi(e^x) = \frac{1}{2\pi} \int_{-a}^a \tilde{\phi}(is) e^{-sx} ds. \quad (7)$$

Because of this,  $\phi(e^x)$  can be extended to an entire function over the complex  $z$ -plane ( $z = x + iy$ ). that is, the function

$$\phi(e^z) = \frac{1}{2\pi} \int_{-a}^a \tilde{\phi}(is) e^{-sz} ds \quad (8)$$

is analytic for all finite  $z$ . This follows from the following facts:

- (i) In integral (8) converge uniformly over every bounded domain of the  $z$ -plane.
- (ii) The integrand is a continuous function of  $(z, s)$  for every complex  $z$  and every real  $s$ .
- (iii) The integrand is a continuous function of  $(z, s)$  for every complex  $z$  and every real  $s$ .

Moreover, if (8) is integrated by parts  $k$  times, we obtain

$$\phi(e^z) = -\frac{1}{2\pi} \int_{-a}^a \frac{(i)^k \tilde{\phi}^{(k)}(is) e^{-sz}}{-z^k} ds$$

$$\text{i.e.} \quad \frac{z^k \phi(e^z)}{i^k} = \frac{1}{2\pi} \int_{-a}^a \tilde{\phi}^{(k)}(is) e^{-sz} ds,$$

$$\text{i.t.} \quad |z^k \phi(e^z)| \leq C_k e^{a|b|}, \quad \text{for all } z \text{ and } k = 0, 1, 2, \dots, \quad (9)$$

$$\text{where} \quad C_k = \frac{1}{2\pi} \int_{-a}^a |\tilde{\phi}^{(k)}(is)| ds.$$

Thus, if  $\phi(is)$  is in  $\mathcal{D}$ , with its support in  $-a \leq s \leq a$ , then  $\phi(e^x)$  can be extended to an entire function and there exists a set of constants  $C_k$  ( $k = 0, 1, 2, \dots$ ), such that (9) is satisfied.

The converse is also true. Indeed,

$$\tilde{\phi}(is) = \int_{-\infty}^{\infty} \phi(e^x) e^{sx} dx$$



nd, with  $\phi(e^z)$  being entire and satisfies (9), the path of integration may be shifted in the  $z$ -plane onto any line which is parallel to the  $x$ -axis. This may be justified by Cauchy's theorem and the fact, that, for all  $y$  in any fixed finite interval,  $\phi(x + iy)$  goes to zero faster than any power of  $1/|x|$  as  $|x| \rightarrow \infty$ , according to (9). Thus by shifting the path of integration, we have, that for every  $y$ ,

$$\begin{aligned}\tilde{\phi}(is) &= \int_{-\infty}^{\infty} \phi(e^{(x+iy)}) e^{s(x+iy)} dx \\ &= e^{isy} \int_{-\infty}^{\infty} \phi(e^{(x+iy)}) e^{sz} dx.\end{aligned}$$

because of (9), the last integral converges uniformly for  $-\infty < x < \infty$ . By formally differentiating under the integral sign, we obtain

$$\begin{aligned}i \tilde{\phi}^{(1)}(is) &= \int_{-\infty}^{\infty} z \phi(e^z) e^{sz} dx \\ &= e^{isy} \int_{-\infty}^{\infty} z \phi(e^z) e^{sz} dx,\end{aligned}\tag{10}$$

where the last integral is again uniformly convergent for  $-\infty < x < \infty$ . Hence  $\tilde{\phi}(is)$  possesses an ordinary first derivative given by (10). Continuation of this process yields that  $\tilde{\phi}(is)$  is infinitely smooth, and

$$(i)^k \tilde{\phi}^{(k)}(is) = \int_{-\infty}^{\infty} z^k \phi(e^z) e^{sz} dx.\tag{11}$$

We shall now show that  $\tilde{\phi}(is)$  has its support contained in the interval  $-a \leq s \leq a$ . By using (9), for both  $k=0$  and  $k=2$ , we may write

$$\begin{aligned}|\phi(e^z)| &\leq e^{a|y|} \inf \left( C_0, \frac{C_2}{|z|^2} \right) \\ &\leq \frac{C e^{a|y|}}{1+x^2},\end{aligned}$$

where  $C$  is still another constant. Consequently, for every  $y$ , we may write

$$|\tilde{\Phi}(s)| \leq e^{isy+a|y|} \int_{-\infty}^{\infty} \frac{C}{1+x^2} dx$$

$$\text{i.e.} \quad |\tilde{\Phi}(is)| \leq C\pi e^{isy+a|y|}. \quad (12)$$

Now, let,  $u < 0$ ,  $u$  being variable, and  $y = \frac{u|s|}{s}$ . Then

$$|\tilde{\Phi}(is)| \leq C\pi e^{u(i|s|-a)}.$$

For  $s > a$ , the right hand side of this inequality goes to zero as  $u \rightarrow \infty$ . This implies that  $|\tilde{\Phi}(is)| = 0$  for  $|s| > a$ . Following lemma may suit to summarize our above discussion.

*Lemma 1* : A necessary and sufficient condition for  $\tilde{\Phi}(is)$  to be in  $\mathcal{D}$ , with its support contained in  $-a \leq s \leq a$ , is that its inverse Mellin transform can be extended to an entire function that satisfies the inequalities (9).

*Proof*:  $\mathcal{Z}$  symbolizes the space of all functions, whose Mellin transforms are elements of  $\mathcal{D}$ . The functions of  $\mathcal{Z}$  will also be called testing functions. Lemma 1 characterizes such functions as,  $\mathcal{Z}$  is the space of all entire functions, that satisfy a set of inequalities of the form (9) for some constants  $C_k$  and  $a$ . Clearly,  $\mathcal{Z}$  is a linear space. Also, the direct and inverse Mellin transformations are linear one-to-one mappings of  $\mathcal{Z}$  onto  $\mathcal{D}$  and  $\mathcal{D}$  onto  $\mathcal{Z}$ , respectively.

By letting  $\tilde{\Phi}(is)$  to be in  $\mathcal{D}$  and by denoting the extension over the  $z$ -plane of the inverse Mellin transform of  $\tilde{\Phi}(is)$  by  $\mathcal{F}_c^{-1} \tilde{\Phi}(is)$ , we have the following formulae, where  $\tau$  is a real constant and  $\alpha$  is a complex constants

$$(-iz)^k \phi(e^z) = \mathcal{F}_c^{-1} [\tilde{\Phi}^{(k)}(is)], \quad (13)$$

$$\phi^{(k)}(e^z) = \mathcal{F}_c^{-1} [(s)^k \phi(is)], \quad (14)$$

$$\phi(e^z) e^{i\tau z} = \mathcal{F}_c^{-1} [\phi(i(s-\tau))], \quad (15)$$

$$\phi(e^{z-i\alpha}) = \mathcal{F}_c^{-1} [e^{\alpha s} \tilde{\Phi}(is)]. \quad (16)$$

Now, in order to describe the concept of convergence in space  $\mathcal{Z}$ , we say that  $\{\phi_v\}_{v=1}^{\infty}$  converges in  $\mathcal{Z}$  if the following conditions are satisfied.

- (i) Each  $\phi_v$  is in  $\mathcal{Z}$ .
- (ii) There exists a set of constants  $a$  and  $C_k$  ( $k = 0, 1, 2, \dots$ ), which do not depend upon  $v$ , such that for all

$$z = x + iy,$$

$$|z^k \phi_v(e^z)| \leq C_k e^{a|k|}, \quad k = 0, 1, 2, \dots \quad (17)$$

- (iii)  $\{\phi_v(e^z)\}_{v=1}^{\infty}$  converges uniformly on every bounded domain of the  $z$ -plane.

As a consequence of this statement, the limit function  $\phi$  of  $\{\phi_v\}_{v=1}^{\infty}$  is also in  $\mathcal{Z}$ ; for it will obviously satisfy the inequalities (17), and the uniformity of the convergence in condition (iii) ensures that  $\phi(e^z)$  is analytic for all  $z$  (Titchmarsh<sup>2</sup>, p. 95). Thus, the space  $\mathcal{Z}$  is closed under convergence.

The conditions (ii) and (iii), together, imply that  $\{x^k \phi_v(e^x)\}_{v=1}^{\infty}$  converges to  $x^k \phi(e^x)$  uniformly for  $-\infty < x < \infty$ .

*Theorem 1* : The sequence  $\{\tilde{\phi}_v\}_{v=1}^{\infty}$  converges in  $\mathcal{D}$  to the limit  $\tilde{\phi}$  iff the inverse Mellin transforms  $\{\phi_v\}_{v=1}^{\infty}$  converge in  $\mathcal{Z}$  to the limit  $\phi = \mathcal{F}^{-1} \tilde{\phi}$ .

*Proof* : Let  $\{\tilde{\phi}_v\}_{v=1}^{\infty}$  converge in  $\mathcal{D}$  to  $\tilde{\phi}$  and let the supports of all the  $\tilde{\phi}_v$  be contained in  $-a \leq s \leq a$ .

Then the  $\phi_v$  and  $\phi$  are in  $\mathcal{Z}$ . Also,

$$|z^k \phi_v(e^z)| = \left| \frac{1}{2\pi} \int_{-a}^a \tilde{\phi}_v^{(k)}(is) e^{-sz} ds \right|$$

$$\begin{aligned}
&\leq \frac{e^{a|y|}}{2\pi} \int_{-a}^a |\tilde{\phi}_v^{(k)}(is)| ds \\
&\leq \frac{a e^{a|y|}}{\pi} \sup_s |\tilde{\phi}_v^{(k)}(is)|.
\end{aligned} \tag{18}$$

Since  $\{\tilde{\phi}_v\}_{v=1}^\infty$  converges to  $\tilde{\phi}$  in  $\mathcal{D}$ ,  $\sup |\tilde{\phi}_v^{(k)}(is)|$  is uniformly bounded for all  $v$ . Thus, the  $\phi_v$  satisfy (17).

The third condition for convergence in  $Z$  is also fulfilled. Indeed, according to (18),

$$|\phi_v(e^z) - \phi(e^z)| \leq \frac{a e^{a|y|}}{\pi} \sup_s |\tilde{\phi}_v(is) - \tilde{\phi}(is)|.$$

But, as  $v \rightarrow \infty$ ,  $\sup |\tilde{\phi}_v(is) - \tilde{\phi}(is)| \rightarrow 0$  and, on each bounded domain of the  $z$ -plane,  $e^{a|y|}$  is bounded. Thus  $|\phi_v(e^z) - \phi(e^z)| \rightarrow 0$  uniformly on each such domain.

Conversely, if  $\{\phi_v\}_{v=1}^\infty$  converges in  $Z$  to  $\phi$ , then by (17) and Lemma 1, all  $\tilde{\phi}_v(is)$  and  $\tilde{\phi}(is)$  are in  $\mathcal{D}$  and they have their supports contained in  $-a \leq s \leq a$ . Also, for each non-negative integer  $k$ ,

$$\begin{aligned}
|\tilde{\phi}_v^{(k)}(is) - \tilde{\phi}^{(k)}(is)| &= \left| \int_{-\infty}^{\infty} z^k [\phi_v(e^z) - \phi(e^z)] e^{sz} dz \right| \\
&\leq \int_{-\infty}^{\infty} \left| \frac{(z^k + z^{k+2}) [\phi_v(e^z) - \phi(e^z)]}{1 + z^2} \right| dz \\
&\leq \pi \sup_z \left| (z^k + z^{k+2}) [\phi_v(e^z) - \phi(e^z)] \right|.
\end{aligned}$$

By conditions (ii) and (iii) of our definition of convergence in  $Z$ , the right side of last relation converges to zero. Thus  $\{\tilde{\phi}_v\}_{v=1}^\infty$  converges in  $\mathcal{D}$  to  $\tilde{\phi}$ .

**Theorem 2 :**  $Z$  is a proper subspace of  $S$ , where  $S$  is the testing function-space of rapid descent.

*Proof:* If  $\phi$  is in  $\mathcal{Z}$ , it is an entire function and hence  $\phi(e^x)$  is infinitely smooth for all  $x$ . Also, its Mellin transform  $\tilde{\phi}(is)$  is in  $\mathcal{D}$ , which implies that  $s^k \tilde{\phi}(is)$  is also in  $\mathcal{D}$ . Therefore, by (14),  $\phi^{(k)}(e^x)$  is again in  $\mathcal{Z}$ , so that for each pair of non-negative integers  $m$  and  $k$

$$|x^k \phi^{(k)}(e^x)| \leq C_{m,k}, \quad -\infty < x < \infty.$$

Hence,  $\phi$  is in  $\mathcal{S}$ .

Finally,  $\mathcal{D}$  is part of  $\mathcal{S}$  and  $\mathcal{D}$  does not intersect  $\mathcal{Z}$ , except for the zero function. Therefore,  $\mathcal{Z}$  is truly a proper subspace of  $\mathcal{S}$ .

It may be advocated that, convergence in  $\mathcal{Z}$  implies convergence in  $\mathcal{S}$ .

*Theorem 3:* If the sequence  $\{\phi_v\}_{v=1}^{\infty}$  converges in  $\mathcal{Z}$  to  $\phi$ , then it also converges in  $\mathcal{S}$  to  $\phi$ .

*Proof:* From theorem 1, it implies that  $\{\tilde{\phi}_v(is)\}_{v=1}^{\infty}$  converges in  $\mathcal{D}$  to  $\tilde{\phi}(is)$ . But then, for  $k = 0, 1, 2, \dots$ ,  $\{s^k \tilde{\phi}_v(is)\}_{v=1}^{\infty}$  converges in  $\mathcal{D}$  to  $s^k \tilde{\phi}(is)$ . Hence  $\{\phi_v^{(k)}(e^x)\}$  converges in  $\mathcal{Z}$  to  $\phi^{(k)}(e^x)$  and, by the definition of convergence in  $\mathcal{Z}$ , for each pair of non-negative integers  $m$  and  $k$ ,  $\{x^m \cdot \phi_v^{(k)}(e^x)\}_{v=1}^{\infty}$  converges to  $x^m \cdot \phi^{(k)}(e^x)$  uniformly for  $-\infty < x < \infty$ , which asserts the theorem.

*Theorem 4:* For each  $\phi$  in  $\mathcal{S}$  there exists a sequence  $\{\phi_v\}_{v=1}^{\infty}$  with elements exclusively in  $\mathcal{Z}$  that converges in  $\mathcal{S}$  to  $\phi$ .

*Proof:* Since the Mellin transformation maps  $\mathcal{S}$  onto itself  $\phi$  is also in  $\mathcal{S}$ . Moreover,  $\mathcal{D}$  is dense in  $\mathcal{S}$ . Therefore, suppose a sequence  $\{\tilde{\phi}_v(is)\}_{v=1}^{\infty}$  of functions in  $\mathcal{D}$ , which converges in  $\mathcal{S}$  to  $\tilde{\phi}$ . By the continuity of the inverse Mellin transformation, as a mapping of  $\mathcal{S}$  onto itself,  $\{\phi_v(e^x)\}_{v=1}^{\infty}$  is the sequence we seek.

We assume that  $\phi(e^x)$  and  $\phi_1(e^x)$  are both in  $\mathcal{Z}$ , so we list out several operations, under which the space  $\mathcal{Z}$  is closed :

- (i) Addition :  $\phi(e^x) + \phi_1(e^x) \in \mathcal{Z}$ .
- (ii) Multiplication by a constant  $\alpha$  :  $\alpha \phi(e^x) \in \mathcal{Z}$ .
- (iii) Shifting :  $\phi(e^{x-\alpha}) \in \mathcal{Z}$ , where  $\alpha$  is a real or complex member.  $\phi(e^{x-\alpha})$  is also defined when  $\alpha$  is complex, because  $\phi$  is an entire function.
- (iv) Transposition :  $\phi(e^{-x}) \in \mathcal{Z}$ .
- (v) Multiplication of the independent variable by a positive constant  $a$  :  $\phi(e^{ax}) \in \mathcal{Z}$ .
- (vi) Differentiation :  $\phi^{(1)}(e^x) \in \mathcal{Z}$ .
- (vii) Multiplication by an entire function  $\psi$  that satisfies an inequality of the form,

$$|\psi(e^z)| \leq C e^{b|z|} (1 + |e^z|^m), \quad (19)$$

where  $C$  and  $b$  are real constants and  $m$  is an integer,  $\psi \phi \in \mathcal{Z}$ .

### The Space $\mathcal{Z}'$ of Ultradistributions for the Mellin Transformation

The ultradistribution for the Mellin transformation can be defined by the Parseval's relation as

$$\left( \tilde{f}(is), \overline{\tilde{\phi}(is)} \right) = \left( f(e^x), \overline{\phi(e^x)} \right), \quad \text{for all } \phi \text{ in } \mathcal{D}, \quad (20)$$

where  $s \in \mathcal{Z}'$  and  $\tilde{f}$  denotes the Mellin transform in the form of Fourier transform.

*Theorem 5* :  $\mathcal{Z}'$  contains  $S'$ , where  $S'$  is the dual of  $S$ .

*Proof* : Since  $\mathcal{Z}$  is the subspace of  $S$  (cf. Theorem 2), hence each distribution of  $f$  of slow growth is linear on  $\mathcal{Z}$ . Furthermore, since convergence in  $\mathcal{Z}$  implies convergence in  $S$ ,  $f$  is also continuous on  $\mathcal{Z}$ .

Here, we deal with the functional and its derivatives and with their other properties in the space  $\mathcal{Z}'$ .

Every ultradistribution  $f$ , that can be related to a locally integrable function  $f(e^x)$  through the relation

$$(f, \phi) = \int_{-\infty}^{\infty} f(e^x) \phi(e^x) dx, \quad (21)$$

where  $\phi$  traverses  $Z$ , is said to be a regular distribution.

If  $f$  is a distribution of slow growth, then a knowledge of  $(f, \phi)$  for every  $\phi$  in  $Z$  determines  $(f, \psi)$  for every  $\psi$  in  $S$ . For  $Z$  is dense in  $S$ ; and consequently, for each  $\psi$  in  $S$ , a sequence  $\{\phi_v\}_{v=1}^{\infty}$  of testing functions in  $Z$  that converges in  $S$  to  $\psi$  can be chosen. Then the limit of  $\{(f, \hat{\phi}_v)\}_{v=1}^{\infty}$  is the value  $(f, \psi)$  that we seek.

Equality for ultradistributions is defined in the usual way. If  $f(e^x)$  and  $g(e^x)$  are ultradistributions and

$$(f(e^x), \phi(e^x)) = (g(e^x), \phi(e^x)), \quad (22)$$

for every  $\phi(e^x)$  in  $Z$ , then  $f(e^x)$  is said to be equal to  $g(e^x)$ .

Now, defining certain operations on ultradistributions, we suppose  $f(e^x)$  and  $g(e^x)$  are ultradistributions and that each relations hold for every testing functions  $\phi(e^x)$  in  $Z$ . The right side expression of the following equations are known values, that are assigned by the definition, to the left side expressions.

(i) The addition of ultradistributions

$$(f(e^x) + g(e^x), \phi(e^x)) = (f(e^x), \phi(e^x)) + (g(e^x), \phi(e^x)). \quad (23)$$

(ii) The multiplication of an ultradistributions by a constant  $\alpha$  :

$$(\alpha f(e^x), \phi(e^x)) = (f(e^x), \alpha \phi(e^x)). \quad (24)$$

The closure of  $Z'$  under these first two operations implies that  $Z'$  is a linear space.

(iii) The shifting of an ultradistribution :

Let  $\alpha$  be a complex constant

$$(f(e^{x-\alpha}), \phi(e^x)) \triangleq (f(e^x), \phi(e^{x+\alpha})). \quad (25)$$

(iv) The transposition of an ultradistribution

$$\left(f(e^{-x}), \phi(e^x)\right) = \left(f(e^x), \phi(e^{-x})\right). \quad (26)$$

(v) The multiplication of the independent variable by a positive constant  $a$

$$\left(f(e^{ax}), \phi(e^x)\right) = \left(f(e^x), \frac{1}{a} \phi(e^{x/a})\right). \quad (27)$$

(vi) The differentiation of an ultradistribution

$$\left(f^{(1)}(e^x), \phi(e^x)\right) \triangleq \left(f(e^x), \phi^{(1)}(e^x)\right). \quad (28)$$

(vii) The multiplication of an ultradistribution by a multiplier in the space  $\mathcal{Z}$ :

Let  $\psi$  be a multiplier in the space  $\mathcal{Z}$ . Then

$$\left(\psi f(e^x), \phi(e^x)\right) = \left(f(e^x), \psi \phi(e^x)\right). \quad (29)$$

The definition of the shifting of an ultradistribution serves to give a meaning to the symbol  $\phi(e^z)$ , where  $z$  is a complex variable ( $x + iy$ ). In accordance with relation (iii),  $f(e^z)$  is defined as follows. For every  $\phi(e^z)$  in  $\mathcal{Z}$ ,

$$\begin{aligned} \left(f(e^z), \phi(e^z)\right) &\triangleq \left(f(e^{x+iy}), \phi(e^x)\right) \\ &\triangleq \left(f(e^x), \phi(e^{x-iy})\right). \end{aligned} \quad (30)$$

In this way  $f(e^x)$  can be extended from the real axis onto the entire  $z$ -plane. In these expressions,  $y$  is held constant, so that the path along which the expression is evaluated is a line running parallel to  $x$ -axis. This will always be understood whenever we write  $f(e^z)$  or  $(f(e^z), \phi(e^z))$ . Thus,  $f(e^z)$  exists as an ultradistribution on each and every line in the  $z$ -plane that is parallel to the  $x$ -axis.

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## Mixed ligand complex formation of $M^{2+}$ ions with quinoline and thymine

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### Abstract

The interaction of  $Mg(II)$ ,  $Mn(II)$ ,  $Co(II)$ ,  $Cu(II)$  and  $Zn(II)$  ions with quinoline, in presence of a pyrimidine base, thymine, has been investigated potentiometrically at  $27^\circ C$  and  $37^\circ C$  and  $0.1M$  ( $NaNO_3$ ) ionic strength. The stability constants of the binary (1:1 & 1:2) and ternary (1:1:1) complexes indicate the stability order as :  $Mn(II) < Mg(II) < Co(II) < Zn(II) < Cu(II)$ .  $\Delta \log K$  values obtained are positive and suggest greater stabilisation of ternary complexes. The calculated values of thermodynamic parameters ( $\Delta G$ ,  $\Delta H$  and  $\Delta S$ ) indicate that the interactions are enthalpy characterised.

(**Keywords** : ternary complexes/ $M^{2+}$ -quinoline-thymine equilibria/stability of quinoline complexes/stability of bivalent metal complexes)

The interaction of biologically active metal ions ( $Mg^{++}$ ,  $Mn^{++}$ ,  $Co^{++}$ ,  $Cu^{++}$ , and  $Zn^{++}$ ) with carcinogenic molecule quinoline (Qnl) in presence of a pyrimidine base, thymine (Tm) is presented in this short notes. All the chemicals used were of high purity A.R. or S.M. grade. Qnl sample was obtained from Aldrich and that of Tm from E. Merk, India. The preparation and standardisation of the metal ions and the ligand solutions, and the experimental details are the same as reported earlier<sup>1</sup>.

Conductometric studies of the metal-drug and metal-Tm equilibria in solution utilising the mono-variation method<sup>2</sup> indicate formation of two complexes in these systems, with the metal-drug or metal-Tm molar ratio 1:1 and 1:2 respectively while the basic ligands in acidic solution show one step of deprotonation of the protonated ligands ( $L + H^+ \rightleftharpoons LH^+$ ); in accordance with the earlier reports<sup>3,4</sup>.

Representative set of experimental titration curves for different  $M^{II}$  : Qnl : Tm systems studied reveal the formation of different  $M^{II}$  : Qnl : Tm 1 : 1 : 1 mixed ligand complexes at pH values (6-10), higher than those corresponding to the formation of the binary

complexes of the drug, in the step-wise manner :  $M + L \xrightleftharpoons{A} [MLA]$ ; where,  $M = Mg(II)$ ,  $Mn(II)$ ,  $Co(II)$ ,  $Cu(II)$ , or  $Zn(II)$  and  $L = Qnl$  and  $A = Tm$ .

Values of  $\log K_n^H$ , and  $\log K_{ML}^M$ ,  $\log K_{ML2}^{ML}$  and  $\log K_{MLA}^{ML}$  (calculated at  $27^\circ$  and  $37^\circ C$  and  $0.1M$   $NaNO_3$ , Table 1, using modified Irving-Rossotti equations<sup>5</sup>) indicate that with the increase in temperature the values of  $\log K_n^H$  and  $\log K_{MLA}^{ML}$  decrease, indicating exothermic

Table 1 – Values of stability constants and thermodynamic parameters  $\mu=0.1\text{M}$  ( $\text{NaNO}_3$ ); Temp. =  $27^\circ\text{C}$  (a) and  $37^\circ\text{C}$  (b).

Constants	H	Mg	Mn	Co	Cu	Zn
$\log K^H$	(a) 4.95 (b) 4.87					
$\log K_{ML}^M$	(a) (b)	2.95 2.47	2.90 2.32	3.65 3.20	4.05 3.80	3.65 3.55
$\log K_{ML_2}^{ML}$	(a) (b)	1.50 1.25 <sup>c</sup>	1.47 1.23	2.00 1.50	3.00 2.05	3.01 1.45
$\log K_{MLA}^{ML}$	(a) (b)	3.39 2.99	3.10 2.71	3.90 3.47	4.16 3.95	3.96 3.65
$\Delta \log K$ $\log (K_{MLA}^{ML} - K_{ML}^M)$		0.52 <sup>b</sup>	0.39 <sup>b</sup>	0.27 <sup>b</sup>	0.15 <sup>b</sup>	0.10 <sup>b</sup>
$-\Delta G$ (K cal/mole)		4.25 <sup>b</sup>	3.85 <sup>b</sup>	4.93 <sup>b</sup>	5.61 <sup>b</sup>	5.19 <sup>b</sup>
$-\Delta H$ ( do )		17.11 <sup>b</sup>	16.68 <sup>b</sup>	18.39 <sup>b</sup>	8.98 <sup>b</sup>	13.26 <sup>b</sup>
$-\Delta S$ (cals/deg/mole)		41.48 <sup>b</sup>	41.38 <sup>b</sup>	43.42 <sup>b</sup>	10.87 <sup>b</sup>	26.03 <sup>b</sup>

nature of complexation reactions. The positive values of the stability qualifying factor,  $\Delta \log K$ , obtained indicate greater stabilisation of ternary complexes<sup>6</sup>, compared to that of the binary ( $\text{ML}_2$ ) complexes (i.e.  $\log K_{MLA}^{ML} > \log K_{ML}^M$ ). The results of the study indicate the possibility of attack of the carcinogenic molecules with nucleic acid through the biologically active metal ions as proposed earlier in the chelate hypothesis of carcinogenesis<sup>7</sup>.

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## A new spot test for the on field detection of dithiocarbamate fungicides

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### Abstract

A new spot test has been developed for the on field detection of dithiocarbamate fungicides at  $\mu\text{g}$  levels in soil, vegetation and water. Copper-ammonia complex on cation-exchange resin beads in presence of diethanolamine has been used as a chromogenic reagent for carbon disulphide.

(Keywords: copper-ammonia complex/cation-exchange resin/dithiocarbamates/fungicides).

Spot test analysis has been found to be extremely useful for the characterization of an analyte<sup>1</sup>. Therefore, in continuation<sup>2</sup> to our previous research work now a new spot test has been developed for the detection of dithiocarbamate fungicides in soil, vegetation and water. The spot test is based on the formation of a brown color complex on cation-exchange resin beads (in the form of  $\text{Cu}(\text{NH}_3)_4^{2+}$ ) with carbon disulphide in presence of diethanolamine.

The following solutions and reagents were prepared as usual: (a) Cuppric acetate (0.8 mg) and diethanolamine (5g) in 50mL of ethanole, (b) nickel acetate (0.9 mg) and diethanolamine (5g) in 50 mL of ethanol, (c) cobalt acetate (0.9 mg) and diethanolamine (5g) in 50mL of ehanol, (d) 5g of morpholine of n-propylamine or diethanolamine or triethanolamine or aniline or diphenylamine or ethylenediaminetetraacetic acid in 50 mL of ethanol, (e) copper ammonia complex,  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  on cation exchange resin beads (CAR) was prepared by treating Towex 50  $\times$  8, 14-52 mesh (CDH Bombay, India) beads in  $\text{H}^+$  form (1g) with cuppric acetate solution (0.1 M), and then with ammonium hydroxide (1:1). The intense blue resin beads so obtained were washed 3-4 times with distilled water, dried at room temperature (30°C) and stored in a coloured glass bottle for use.

Soil samples were collected from village Jawar (Iglas) Aligarh, dried, sized and stored as usual<sup>2</sup>. Leaves of onion, potato, mustard, banayan and neem were collected from Khawaja Krishi Farm, Aligarh in the month of November 1998. The samples were stored at 4°C and tested in 24 h.

The test material (0.1 mL or 100 mg) was taken in a test tube A (9.8  $\times$  1.2 cm i.d.) jointed with a side U-tube<sup>3</sup> (16.9  $\times$  0.3 c, i.d.) (Fig. 1). The moisture contents were removed by heating. The contents were cooled to room temperature, and 0.1 mL of 10 M  $\text{H}_2\text{SO}_4$

was added to it. The reagents (0.1 mL) (a) or (b) or (c) or 4-5 beads of CAR and 0.1 mL of diethanolamine solution was taken in the side U tube. The tube A was stoppered and heated to bubble the fumes  $\text{CS}_2$  through U tube containing the reagent. The change in colour after 1 min. as well as after 5 min. was noted.

The lower detection limit (LDL) was measured by taking the known volume (0.1 mL) of the standard solutions of different concentrations. A soil sample (5 g) was treated with aqueous suspension of mancozeb (1 mL of 0.06%–1%) in glass petridish. The contents were thoroughly mixed and placed at room temperature. Similarly, vegetation samples were treated with mancozeb. Mancozeb was detected in these samples by using the above mentioned procedure.

It is well known that carbon disulphide reacts with transitional metal salts in presence of several primary and secondary amines to give transitional metal dithiocarbamate complexes<sup>4</sup>. Many transitional metal-dithiocarbamates have been used as catalysts in vulcanization of rubber<sup>5</sup> and in copolymerization of acrylate and styrene<sup>6</sup>, fungicides<sup>7-10</sup>, additives in lubricating oils<sup>11</sup>, inhibitors<sup>12-14</sup> in a number of cells, absorbents<sup>15,16</sup> to enrich metal ions and organics in water, extractants<sup>17,18</sup> to enrich metal ions in sea water and in biological fluids, collectors in floatation<sup>19,20</sup> of non-ferrous metals and chromogenic reagents in coulometry/spectrophotometry<sup>1,21,22</sup>. The following results manifest that this new reagent, cation exchange resin beads in  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  form-diethanolamine (CAR), is more sensitive as well as selective.

The sensitivity for detection of mancozeb was found to be in the following sequences: (a) when CAR was used in presence of different amines and (b) when DEA was used in presence of different salts.

(a) diethanolamine > triethanolamine > morpholine > n-propylamine

(b) CAR > copper acetate > nickel acetate > cobalt acetate.

CAR gives no colour with carbon disulphide in presence of diphenylamine, ethylenediaminetetra acetic acid and aniline. The colour intensity was maximum in the pH range 4.99–5.89 than that at pH 4 or 10. It is observed that mancozeb gives brown colour with CAR-DEA while it gives yellow colour with copper (II) acetate-DEA. The brown colour is easy to visualize and its sensitivity is higher (4.5  $\mu\text{g}/0.1 \text{ mL}$ ) than that of yellow colour (10  $\mu\text{g}/0.1 \text{ mL}$ ). The response of the spot test was tested for different types of compounds. The test was also performed to test mancozeb in presence of several foreign substances. The results obtained are given in Table 1. The results show that most of the foreign substances do not produce any colour as well as they do not interfere in the detection of mancozeb i.e. no masking of the colour or no appreciable increase in the intensity of

Table 1 – Detection of mancozeb (1 mg) in presence of foreign substances.

Compound	Colour		Compound	Colour	
	1 min.	5 min.		1 min	5 min
Barbituric	LY	DBr	<i>A. ACIDS</i>		
Hippuric (LY)	LY	DY	Gallic	LY	Y
Malic	LGrY	DBr	Isocitric	VLY	GrLy
Succinic	LGrY	DBr	Phthalic	LY	Br
Tartaric	DY	Br	Sulphanilic	Y	DY
1-Butanol	Y	Br	<i>B. ALCOHOLS</i>		
Methanol	Y	Br	Ethanol	Y	Br
Benzaldehyde	Y	Br	1-Propanol	Y	Br
m-Nitrobenzaldehyde	LY	Br	<i>C. ALDEHYDES</i>		
Vanillin	VLY	LY	4-Dimethylaminobenzaldehyde	VLY	Br
Aniline	LY	GrY	<i>D. AMINES</i>		
Indole	LY	Y	Diethylaniline	LGrY	Br
Trimethylamine	LY	DY	Nicotine	DY	Br
Dimethylformamide	VLY	LY	<i>E. AMIDES</i>		
Thiourea	Y	DY	Salicylamide	LY	DY
Diethylether	LY	DY	Urea	Y	Br
Pyridine	Y	Br	<i>F. ETHER</i>		
			<i>G. HETEROCYCLIC BASE</i>		





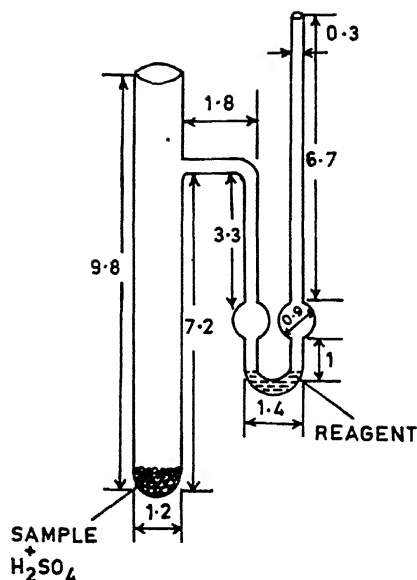


Fig. 1 – Apparatus for detection of mancozeb. All the dimensions are in cm.

the colour. However, leaves of bakayan, bathua and mustard, onion and tomato give light yellow colour with the reagent (CAR-DEA). So there is a slight increase in the intensity of the brown colour produced with mancozeb.

The spot test under study was successfully used to detect dimethyldithiocarbamates and morpholine dithiocarbamates of Zn(II), Mn(II), Cu(II) and Fe(III) at trace levels (4–10  $\mu$ /1.0 mL) in soil, vegetation and water.

The present study shows that the use of cation-exchange resin beads in copper ammonia complex form in place of cupric acetate makes the test more sensitive. The test can be successfully used for the detection of traces of dithiocarbamate fungicides in soil directly.

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## Study of metal-drug equilibria in solution

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### Abstract

Equilibrium studies on the mixed ligand complex formation of  $M^{2+}$  ( $M = \text{Mg, Mn, Co, Cu and Zn}$ ) with methotrexate (MTX) in the presence of thymine (Tm) at  $27^\circ$  and  $37^\circ$  and  $0.1\text{M}$  ( $\text{NaNO}_3$ ) ionic strength indicated the order of stability as  $\text{Mn}^{2+} < \text{Mg}^{2+} < \text{Co}^{2+} < \text{Zn}^{2+} < \text{Cu}^{2+}$ .  $\Delta \log K$  values obtained are positive and suggest favoured formation of ternary complexes. Thermodynamic parameters ( $\Delta G$ ,  $\Delta H$  and  $\Delta S$ ) calculated at  $37^\circ$  and  $0.1\text{M}$  ( $\text{NaNO}_3$ ) ionic strength indicate the interactions enthalpy characterised.

(Keywords : metal-drug equilibria/ternary complexes)

Methotrexate (MTX), an important antimetabolite used in the treatment of acute leukemia, Hodgkin's disease, Burkitt's lymphoma and carcinocarcinoma, competitively inhibits enzyme foliate reductase. The mechanism of the block of enzymatic step (during folate metabolism) by the drug can be understood in the light of its strong chelate forming tendency<sup>1-3</sup>. The study of binary chelates of MTX and thymine (Tm) indicated formation of (M:L) only 1:1 and 1:2 complexes with the biologically active metal ions, in accordance with the earlier reported results<sup>1-8</sup>. In this short note is reported the results of the mixed ligand complex formation equilibria of  $M^{2+}$  ions ( $= \text{Mg, Mn, Cu, Co and Zn}$ ) with MTX as primary ligand and Tm as secondary ligand with a view to study the interaction of biologically active metal ions with the anticancer drug (MTX) in presence of a pyrimidine base thymine (Tm) utilising the modified Irving-Rossotti pH titration technique<sup>9</sup>. This may yield useful information for elucidating the molecular mechanism of the activity of anticancer drugs in the light of the chelate hypothesis of drug action<sup>10</sup>.

All the chemicals used were of high purity A.R. or Sarabhai-Merck grade. MTX sample was obtained from Lederle, N.Y. and Tm from E.Merck, India. Solutions of MTX were prepared in double distilled water and neutralised to pH 7 with dilute  $\text{HNO}_3$ ; while Tm solutions were prepared by dissolving it in minimum quantity of dilute  $\text{HNO}_3$ . These solutions were then diluted with double distilled water to required volume. The experimental details are the same as reported earlier<sup>1</sup>. For pH titrations, the following thermostated mixtures (total volume 50 ml,  $\mu 0.1\text{M}$   $\text{NaNO}_3$ ) were titrated with a carbonate-free  $0.1\text{M}$  NaOH solution: (a) 10 ml  $0.04\text{M}$   $\text{HNO}_3$  +  $1\text{M}$   $\text{NaNO}_3$  (b) Mixture (a) + 5 ml  $0.004\text{M}$  MTX, (c) Mixture (a) + 5 ml  $0.004\text{M}$  Tm, (d) Mixture (b) + 10 ml  $0.002\text{M}$  metal, (e) Mixture (c) + 10 ml  $0.002\text{M}$  metal, (f) Mixture (b) + 5 ml  $0.004\text{M}$  Tm, (g) Mixture (f) + 10 ml  $0.002\text{M}$  metal.

Table 1 – Stability constants and thermodynamic parameters  $\mu=0.1M$  ( $NaNO_3$ ); Temp. =  $270^\circ C(a)$ ,  $37^\circ C(b)$ .

Constants	H	Mg	Mn	Co	Cu	Zn
$\log K_1^H$	(a) 9.05 (b) 8.67					
$\log K_2^H$	(a) 3.50 (b) 3.36					
$\log K_{ML}^M$	(a) (b)	7.10 6.30	6.32 5.95	7.27 6.92	7.72 7.22	6.90 6.50
$\log K_{ML_2}^{ML}$	(a) (b)	5.62 3.85	5.45 3.65	6.61 3.87	5.62 4.97	5.95 5.00
$\log K_{MLA}^{ML}$	(a) (b)	6.95 6.42	6.48 6.20	7.60 7.30	8.20 7.66	7.85 7.45
$\Delta \log K$ $\log (K_{MLA}^{ML} - K_{ML}^M)$		0.62 <sup>b</sup>	0.25 <sup>b</sup>	0.38 <sup>b</sup>	0.44 <sup>b</sup>	0.85 <sup>b</sup>
$-\Delta G$ (Kcal/mole)		9.12 <sup>b</sup>	8.81 <sup>b</sup>	10.37 <sup>b</sup>	10.88 <sup>b</sup>	10.58 <sup>b</sup>
$-\Delta H$ (do)		22.67 <sup>b</sup>	11.98 <sup>b</sup>	12.83 <sup>b</sup>	23.10 <sup>b</sup>	17.11 <sup>b</sup>
$-\Delta S$ (Cal/deg/mole)		43.70 <sup>b</sup>	10.22 <sup>b</sup>	7.93 <sup>b</sup>	39.42 <sup>b</sup>	21.06 <sup>b</sup>

Conductometric studies of the metal-drug and metal-Tm equilibria in solution utilising Nair and Pande's mono-variation method<sup>11</sup> indicated formation of two complexes in these systems with the metal-MTX or metal-Tm molar ratio 1 : 1 and 1 : 2 respectively.

Representative set of experimental titration curves, obtained according to the sequence for different  $M^{2+}$  : Tm reveals that below pH 6.8 formation of different  $M^{2+}$  : drug (MTX) binary complexes takes place. This is clear from the appeared divergence of each of the 1:1 binary  $M^{2+}$  – MTX titration curve from that of the corresponding free drug curve in the pH 5-9 region. Beyond these pH values, hydrolysis of the complexes leads to the formation of hydroxocomplex species. Careful examination of titration curves of the ternary complex reveals that the 1 : 1 : 1 mixed ligand complexes are formed at pH values higher than those corresponding to the formation of the binary complexes of the drug in the stepwise manner. The binary complex ML is first formed and it coordinates with Tm (A) as secondary ligand to yield the mixed ligand complex MLA,





The values of  $\log K_{ML}^M$ ,  $\log K_{ML2}^{ML}$  and  $\log K_{MLA}^{ML}$  reported in Table 1 calculated at 27° and 37° and  $\mu = 0.1M$   $NaNO_3$  using modified Irving-Rossotti equations<sup>9</sup> revealed that with the increase in temperature the values of  $\log K_{ML}^M$  and  $\log K_{MLA}^{ML}$  decrease, indicating exothermic nature of complexation reactions. The ternary complexes are characterised by high stability compared to the corresponding M(II)- drug binary complexes, i.e.,  $K_{ML}^M < K_{MLA}^{ML}$ . The  $\Delta \log K$  values obtained are positive indicating greater stabilisation of the drug (Table 1). The order of stability with reference to metal ions is :  $Mn^{2+} < Mg^{2+} < Co^{2+} < Zn^{2+} < Cu^{2+}$ , while the thermodynamic parameters ( $\Delta G$ ,  $\Delta H$  and  $\Delta S$ ) calculated at 37° and 0.1M ( $NaNO_3$ ) ionic strength indicate the interactions enthalpy characterised (Table 1).

Thus the results of the present study support the possibility of formation of metal bridged drug-receptor chelates during the activity of anticancer drugs proposed earlier<sup>10</sup>.

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